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(54) **METHODS OF FORMING AN ARRAY OF OPENINGS IN A SUBSTRATE, AND RELATED METHODS OF FORMING A SEMICONDUCTOR DEVICE STRUCTURE**

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(58) **Field of Classification Search**

USPC 257/622, E21.24, E21.259; 438/424, 438/780

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,623,674	A	11/1986	Bailey
4,797,357	A	1/1989	Mura et al.
4,818,713	A	4/1989	Feygenson
4,877,647	A	10/1989	Klabunde
5,328,810	A	7/1994	Lowrey et al.
5,374,367	A	12/1994	Edamura et al.
5,382,373	A	1/1995	Carlson
5,482,656	A	1/1996	Hiraoka et al.
5,512,131	A	4/1996	Kumar et al.

(Continued)

FOREIGN PATENT DOCUMENTS

CN	1562730	A	1/2005
CN	1799131	A	7/2006

(Continued)

OTHER PUBLICATIONS

Fujita et al., Thin Silica Film with a Network Structure as Prepared by Surface Sol-Gel Transcription on the Poly(styrene-b-4-vinylpyridine) Polymer Film, Chemistry Letters, vol. 32, No. 4, Dec. 31, 2003, pp. 352-353.

(Continued)

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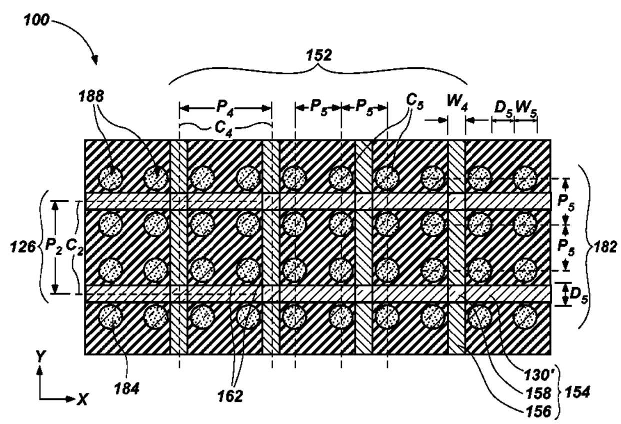
(57) **ABSTRACT**

A method of forming an array of openings in a substrate. The method comprises forming a template structure comprising a plurality of parallel features and a plurality of additional parallel features perpendicularly intersecting the plurality of additional parallel features of the plurality over a substrate to define wells, each of the plurality of parallel features having substantially the same dimensions and relative spacing as each of the plurality of additional parallel features. A block copolymer material is formed in each of the wells. The block copolymer material is processed to form a patterned polymer material defining a pattern of openings. The pattern of openings is transferred to the substrate to form an array of openings in the substrate. A method of forming a semiconductor device structure, and a semiconductor device structure are also described.

21 Claims, 10 Drawing Sheets



(56) **References Cited**

U.S. PATENT DOCUMENTS

5,538,655	A	7/1996	Fauteux et al.
5,580,700	A	12/1996	Rahman
5,620,850	A	4/1997	Bamdad et al.
5,622,668	A	4/1997	Thomas et al.
5,772,905	A	6/1998	Chou
5,834,583	A	11/1998	Hancock et al.
5,849,810	A	12/1998	Müller
5,879,582	A	3/1999	Havelka et al.
5,879,853	A	3/1999	Azuma
5,891,356	A	4/1999	Inoue et al.
5,904,824	A	5/1999	Oh et al.
5,925,259	A	7/1999	Biebuyck et al.
5,948,470	A	9/1999	Harrison et al.
5,958,704	A	9/1999	Starzl et al.
6,051,869	A	4/2000	Pan et al.
6,111,323	A	8/2000	Carter et al.
6,143,647	A	11/2000	Pan et al.
6,153,495	A	11/2000	Kub et al.
6,207,787	B1	3/2001	Fahey et al.
6,251,791	B1	6/2001	Tsai et al.
6,270,946	B1	8/2001	Miller
6,309,580	B1	10/2001	Chou
6,310,138	B1	10/2001	Yonezawa et al.
6,312,971	B1	11/2001	Amundson et al.
6,368,871	B1	4/2002	Christel et al.
6,403,382	B1	6/2002	Zhu et al.
6,414,164	B1	7/2002	Afzali-Ardakani et al.
6,423,465	B1	7/2002	Hawker et al.
6,423,474	B1	7/2002	Holscher
6,503,841	B1	1/2003	Criscuolo et al.
6,506,660	B2	1/2003	Holmes et al.
6,517,933	B1	2/2003	Soane et al.
6,518,194	B2	2/2003	Winningham et al.
6,537,920	B1	3/2003	Krivokapic
6,548,830	B1	4/2003	Noguchi et al.
6,565,763	B1	5/2003	Asakawa et al.
6,565,764	B2	5/2003	Hiraoka et al.
6,566,248	B1	5/2003	Wang et al.
6,569,528	B2	5/2003	Nam et al.
6,573,030	B1	6/2003	Fairbairn et al.
6,592,764	B1	7/2003	Stucky et al.
6,630,520	B1	10/2003	Bruza et al.
6,635,912	B2	10/2003	Ohkubo
6,656,308	B2	12/2003	Hougham et al.
6,679,996	B1	1/2004	Yao
6,682,660	B2	1/2004	Sucholeiki et al.
6,689,473	B2	2/2004	Guire et al.
6,699,797	B1	3/2004	Morris et al.
6,713,238	B1	3/2004	Chou et al.
6,746,825	B2	6/2004	Nealey et al.
6,767,693	B1	7/2004	Okoroanyanwu
6,780,492	B2	8/2004	Hawker et al.
6,781,166	B2	8/2004	Lieber et al.
6,797,202	B2	9/2004	Endo et al.
6,809,210	B2	10/2004	Chandross
6,812,132	B2	11/2004	Ramachandrarao et al.
6,825,358	B2	11/2004	Afzali-Ardakani et al.
6,884,842	B2	4/2005	Soane et al.
6,887,332	B1	5/2005	Kagan et al.
6,890,624	B1	5/2005	Kambe et al.
6,890,703	B2	5/2005	Hawker et al.
6,908,861	B2	6/2005	Sreenivasan et al.
6,911,400	B2	6/2005	Colburn et al.
6,913,697	B2	7/2005	Lopez et al.
6,924,341	B2	8/2005	Mays et al.
6,926,953	B2	8/2005	Nealey et al.
6,940,485	B2	9/2005	Noolandi
6,946,332	B2	9/2005	Loo et al.
6,949,456	B2	9/2005	Kumar
6,952,436	B2	10/2005	Wirnsberger et al.
6,957,608	B1	10/2005	Hubert et al.
6,962,823	B2	11/2005	Empedocles et al.
6,989,426	B2	1/2006	Hu
6,992,115	B2	1/2006	Hawker et al.
6,995,439	B1	2/2006	Hill et al.
6,998,152	B2	2/2006	Uhlenbrock
7,001,795	B2	2/2006	Jiang et al.
7,009,227	B2	3/2006	Patrick et al.
7,030,495	B2	4/2006	Colburn et al.
7,037,738	B2	5/2006	Sugiyama et al.
7,037,744	B2	5/2006	Colburn et al.
7,045,851	B2	5/2006	Black et al.
7,056,455	B2	6/2006	Matyjaszewski et al.
7,056,849	B2	6/2006	Wan et al.
7,060,774	B2	6/2006	Sparrowe et al.
7,066,801	B2	6/2006	Balijepalli et al.
7,077,992	B2	7/2006	Sreenivasan et al.
7,087,267	B2	8/2006	Breen et al.
7,090,784	B2	8/2006	Asakawa et al.
7,112,617	B2	9/2006	Kim
7,115,305	B2	10/2006	Bronikowski et al.
7,115,525	B2	10/2006	Abatchev et al.
7,115,995	B2	10/2006	Wong
7,118,784	B1	10/2006	Xie
7,119,321	B2	10/2006	Quinlan
7,132,370	B2	11/2006	Paraschiv et al.
7,135,144	B2	11/2006	Christel et al.
7,135,241	B2	11/2006	Ferraris et al.
7,135,388	B2	11/2006	Ryu et al.
7,135,523	B2	11/2006	Ho et al.
7,151,209	B2	12/2006	Empedocles et al.
7,163,712	B2	1/2007	Chilkoti et al.
7,166,304	B2	1/2007	Harris et al.
7,172,953	B2	2/2007	Lieber et al.
7,186,613	B2	3/2007	Kirner et al.
7,189,430	B2	3/2007	Ajayan et al.
7,189,435	B2	3/2007	Tuominen et al.
7,190,049	B2	3/2007	Tuominen et al.
7,195,733	B2	3/2007	Rogers et al.
7,202,308	B2	4/2007	Boussand et al.
7,208,836	B2	4/2007	Manning
7,252,791	B2	8/2007	Wasserscheid et al.
7,259,101	B2	8/2007	Zurcher et al.
7,279,396	B2	10/2007	Derderian et al.
7,282,240	B1	10/2007	Jackman et al.
7,291,284	B2	11/2007	Mirkin et al.
7,311,943	B2	12/2007	Jacobson et al.
7,326,514	B2	2/2008	Dai et al.
7,332,370	B2	2/2008	Chang et al.
7,332,627	B2	2/2008	Chandross et al.
7,338,275	B2	3/2008	Choi et al.
7,347,953	B2	3/2008	Black et al.
7,368,314	B2	5/2008	Ufert
7,407,887	B2	8/2008	Guo
7,408,186	B2	8/2008	Merkulov et al.
7,419,772	B2	9/2008	Watkins et al.
7,470,954	B2	12/2008	Lee et al.
7,514,339	B2	4/2009	Yang et al.
7,521,090	B1	4/2009	Cheng et al.
7,553,760	B2	6/2009	Yang et al.
7,569,855	B2	8/2009	Lai
7,585,741	B2	9/2009	Manning
7,592,247	B2	9/2009	Yang et al.
7,605,081	B2	10/2009	Yang et al.
7,632,544	B2	12/2009	Ho et al.
7,655,383	B2	2/2010	Mela et al.
7,658,773	B2	2/2010	Pinnow
7,700,157	B2	4/2010	Bronikowski et al.
7,723,009	B2	5/2010	Sandhu et al.
7,767,099	B2	8/2010	Li et al.
7,888,228	B2	2/2011	Blanchard
7,959,975	B2	6/2011	Millward
7,964,107	B2	6/2011	Millward
8,039,196	B2	10/2011	Kim et al.
8,080,615	B2	12/2011	Millward
8,083,953	B2	12/2011	Millward et al.
8,083,958	B2	12/2011	Li et al.
8,097,175	B2	1/2012	Millward et al.
8,101,261	B2	1/2012	Millward et al.
8,114,300	B2	2/2012	Millward
8,114,301	B2	2/2012	Millward et al.
8,114,306	B2	2/2012	Cheng et al.
8,206,601	B2	6/2012	Bosworth et al.
8,287,749	B2	10/2012	Hasegawa et al.

(56) **References Cited**

U.S. PATENT DOCUMENTS

8,294,139	B2	10/2012	Marsh et al.
8,372,295	B2	2/2013	Millward
8,394,483	B2	3/2013	Millward
8,404,124	B2	3/2013	Millward et al.
8,409,449	B2	4/2013	Millward et al.
8,425,982	B2	4/2013	Regner
8,426,313	B2	4/2013	Millward et al.
8,445,592	B2	5/2013	Millward
2001/0024768	A1	9/2001	Matsuo et al.
2001/0049195	A1	12/2001	Chooi et al.
2002/0055239	A1	5/2002	Tuominen et al.
2002/0084429	A1	7/2002	Craighead et al.
2002/0158342	A1	10/2002	Tuominen et al.
2002/0167117	A1	11/2002	Chou
2003/0010241	A1	1/2003	Fujihira et al.
2003/0034329	A1	2/2003	Chou
2003/0068639	A1	4/2003	Haneder et al.
2003/0077452	A1	4/2003	Guire et al.
2003/0080471	A1	5/2003	Chou
2003/0080472	A1	5/2003	Chou
2003/0091752	A1	5/2003	Nealey et al.
2003/0100822	A1	5/2003	Lew et al.
2003/0108879	A1	6/2003	Klaerner et al.
2003/0143375	A1	7/2003	Noguchi et al.
2003/0157248	A1	8/2003	Watkins et al.
2003/0178707	A1	9/2003	Abbott
2003/0180522	A1	9/2003	DeSimone et al.
2003/0180966	A1	9/2003	Abbott et al.
2003/0185741	A1	10/2003	Matyjaszewski
2003/0222048	A1	12/2003	Asakawa et al.
2003/0235930	A1	12/2003	Bao et al.
2004/0023287	A1	2/2004	Harnack et al.
2004/0028875	A1	2/2004	Van Rijn et al.
2004/0058059	A1	3/2004	Linford et al.
2004/0084298	A1	5/2004	Yao et al.
2004/0109263	A1	6/2004	Suda et al.
2004/0124092	A1	7/2004	Black
2004/0125266	A1	7/2004	Miyauchi et al.
2004/0127001	A1	7/2004	Colburn et al.
2004/0142578	A1	7/2004	Wiesner et al.
2004/0159633	A1	8/2004	Whitesides et al.
2004/0163758	A1	8/2004	Kagan et al.
2004/0175628	A1	9/2004	Nealey et al.
2004/0192013	A1	9/2004	Ryu et al.
2004/0222415	A1	11/2004	Chou et al.
2004/0242688	A1	12/2004	Chandross et al.
2004/0254317	A1	12/2004	Hu
2004/0256615	A1	12/2004	Sirringhaus et al.
2004/0256662	A1	12/2004	Black et al.
2004/0265548	A1	12/2004	Ho et al.
2005/0008828	A1	1/2005	Libera et al.
2005/0062165	A1	3/2005	Saenger et al.
2005/0074706	A1	4/2005	Bristol et al.
2005/0079486	A1	4/2005	Abbott et al.
2005/0100830	A1	5/2005	Xu et al.
2005/0120902	A1	6/2005	Adams et al.
2005/0124135	A1	6/2005	Ayazi et al.
2005/0133697	A1	6/2005	Potyrailo et al.
2005/0147841	A1	7/2005	Tavkhelidze
2005/0167651	A1	8/2005	Merkulov et al.
2005/0176256	A1	8/2005	Kudelka
2005/0208752	A1	9/2005	Colburn et al.
2005/0238889	A1	10/2005	Iwamoto et al.
2005/0238967	A1	10/2005	Rogers et al.
2005/0250053	A1	11/2005	Marsh et al.
2005/0271805	A1	12/2005	Kambe et al.
2005/0272341	A1	12/2005	Colburn et al.
2006/0013956	A1	1/2006	Angelescu et al.
2006/0014001	A1	1/2006	Zhang et al.
2006/0024590	A1	2/2006	Sandhu
2006/0030495	A1	2/2006	Gregg
2006/0035387	A1	2/2006	Wagner et al.
2006/0038182	A1	2/2006	Rogers et al.
2006/0046079	A1	3/2006	Lee et al.
2006/0046480	A1	3/2006	Guo
2006/0060863	A1	3/2006	Lu et al.
2006/0062867	A1	3/2006	Choi et al.
2006/0078681	A1	4/2006	Hieda et al.
2006/0097134	A1	5/2006	Rhodes
2006/0105562	A1	5/2006	Yi
2006/0124467	A1	6/2006	Ho et al.
2006/0128165	A1	6/2006	Theiss et al.
2006/0134556	A1	6/2006	Nealey et al.
2006/0137554	A1	6/2006	Kron et al.
2006/0141222	A1	6/2006	Fischer et al.
2006/0141245	A1	6/2006	Stellacci et al.
2006/0154466	A1	7/2006	Lee et al.
2006/0163646	A1	7/2006	Black et al.
2006/0192283	A1	8/2006	Benson
2006/0205875	A1	9/2006	Cha et al.
2006/0211871	A1	9/2006	Dai
2006/0217285	A1	9/2006	Destarac
2006/0228635	A1	10/2006	Suleski
2006/0231525	A1	10/2006	Asakawa et al.
2006/0249784	A1	11/2006	Black et al.
2006/0249796	A1	11/2006	Tavkhelidze
2006/0254440	A1	11/2006	Choi et al.
2006/0255505	A1	11/2006	Sandhu et al.
2006/0257633	A1	11/2006	Inoue et al.
2006/0258159	A1	11/2006	Colburn et al.
2006/0278158	A1	12/2006	Tolbert et al.
2006/0281266	A1	12/2006	Wells
2006/0286305	A1	12/2006	Thies et al.
2006/0286490	A1	12/2006	Sandhu et al.
2006/0292777	A1	12/2006	Dunbar
2007/0020749	A1	1/2007	Nealey et al.
2007/0023247	A1	2/2007	Ulicny et al.
2007/0023805	A1	2/2007	Wells et al.
2007/0045562	A1	3/2007	Parekh
2007/0045642	A1	3/2007	Li
2007/0071881	A1	3/2007	Chua et al.
2007/0072403	A1	3/2007	Sakata
2007/0122749	A1	5/2007	Fu et al.
2007/0122932	A1	5/2007	Kodas et al.
2007/0138131	A1	6/2007	Burdinski
2007/0161237	A1	7/2007	Lieber et al.
2007/0175859	A1	8/2007	Black et al.
2007/0181870	A1	8/2007	Libertino et al.
2007/0183035	A1	8/2007	Asakawa et al.
2007/0194403	A1	8/2007	Cannon et al.
2007/0200477	A1	8/2007	Tuominen et al.
2007/0208159	A1	9/2007	McCloskey et al.
2007/0218202	A1	9/2007	Ajayan et al.
2007/0222995	A1	9/2007	Lu
2007/0224819	A1	9/2007	Sandhu
2007/0224823	A1	9/2007	Sandhu
2007/0227383	A1	10/2007	Decre et al.
2007/0249117	A1	10/2007	Kang et al.
2007/0272951	A1	11/2007	Lieber et al.
2007/0281220	A1	12/2007	Sandhu
2007/0289943	A1	12/2007	Lu et al.
2007/0293041	A1	12/2007	Yang
2008/0032238	A1	2/2008	Lu et al.
2008/0038923	A1	2/2008	Edelstein et al.
2008/0041818	A1	2/2008	Kihara et al.
2008/0047930	A1	2/2008	Blanchet et al.
2008/0064217	A1	3/2008	Horii
2008/0073743	A1	3/2008	Alizadeh et al.
2008/0083991	A1	4/2008	Yang et al.
2008/0085601	A1	4/2008	Park et al.
2008/0093743	A1	4/2008	Yang et al.
2008/0102252	A1	5/2008	Black et al.
2008/0103256	A1	5/2008	Kim et al.
2008/0113169	A1	5/2008	Cha et al.
2008/0164558	A1	7/2008	Yang et al.
2008/0174726	A1	7/2008	Kim
2008/0176767	A1	7/2008	Millward
2008/0193658	A1	8/2008	Millward
2008/0217292	A1	9/2008	Millward et al.
2008/0233297	A1	9/2008	de Jong et al.
2008/0233323	A1	9/2008	Cheng et al.
2008/0257187	A1	10/2008	Millward
2008/0260941	A1	10/2008	Jin
2008/0274413	A1	11/2008	Millward

(56) **References Cited**

U.S. PATENT DOCUMENTS

2008/0286659	A1	11/2008	Millward
2008/0311347	A1	12/2008	Millward et al.
2008/0315270	A1	12/2008	Marsh et al.
2008/0318005	A1	12/2008	Millward
2009/0062470	A1	3/2009	Millward et al.
2009/0155579	A1	6/2009	Greco et al.
2009/0200646	A1	8/2009	Millward et al.
2009/0206489	A1	8/2009	Li et al.
2009/0212016	A1	8/2009	Cheng et al.
2009/0218567	A1	9/2009	Mathew et al.
2009/0236309	A1	9/2009	Millward et al.
2009/0240001	A1	9/2009	Regner
2009/0263628	A1	10/2009	Millward
2009/0267058	A1	10/2009	Namdas et al.
2009/0274887	A1	11/2009	Millward et al.
2009/0317540	A1	12/2009	Sandhu et al.
2010/0092873	A1	4/2010	Sills et al.
2010/0102415	A1	4/2010	Millward et al.
2010/0124826	A1	5/2010	Millward et al.
2010/0137496	A1	6/2010	Millward et al.
2010/0163180	A1	7/2010	Millward
2010/0204402	A1	8/2010	Millward et al.
2010/0279062	A1	11/2010	Millward et al.
2010/0316849	A1	12/2010	Millward et al.
2010/0323096	A1	12/2010	Sills et al.
2011/0232515	A1	9/2011	Millward
2012/0028471	A1	2/2012	Oyama et al.
2012/0122292	A1	5/2012	Sandhu et al.
2012/0133017	A1	5/2012	Millward et al.
2012/0135159	A1	5/2012	Xiao et al.
2012/0138570	A1	6/2012	Millward et al.
2012/0164389	A1	6/2012	Yang et al.
2012/0202017	A1	8/2012	Nealey et al.
2012/0211871	A1	8/2012	Russell et al.
2012/0223053	A1	9/2012	Millward et al.
2012/0225243	A1	9/2012	Millward
2013/0295323	A1	11/2013	Millward
2013/0330668	A1	12/2013	Wu et al.
2013/0330688	A1	12/2013	Hedrick et al.
2014/0060736	A1	3/2014	Millward et al.

FOREIGN PATENT DOCUMENTS

CN	101013662	A	8/2007
EP	0784543		4/2000
EP	1416303	A2	5/2004
EP	1906237	A2	4/2008
EP	1593164	B1	6/2010
JP	11080414	A	3/1999
JP	2003155365		5/2003
JP	2004335962		11/2004
JP	2005008882	A	1/2005
JP	2005029779	A	2/2005
JP	2006036923	A	2/2006
JP	2006055982	A	3/2006
JP	2006110434	A	4/2006
JP	2007194175		8/2007
JP	2008036491	A	2/2008
KR	1020060128378	A	12/2006
KR	20070029762		3/2007
KR	100771886	B1	11/2007
TW	200400990		3/1992
TW	200633925		10/1994
TW	200740602		1/1996
TW	584670	B	4/2004
TW	200419017		10/2004
TW	200511364		3/2005
TW	256110		6/2006
TW	I253456		11/2007
TW	200802421		1/2008
WO	9007575		7/1990
WO	9706013	A1	2/1997
WO	9839645	A1	9/1998
WO	9947570	A1	9/1999
WO	0031183	A1	6/2000
WO	0218080	A1	3/2002
WO	02081372	A2	10/2002
WO	03045840	A2	6/2003
WO	2005122285	A2	12/2005
WO	2006003592	A2	1/2006
WO	2006003594	A2	1/2006
WO	2006076016	A2	7/2006
WO	2006078952	A1	7/2006
WO	2006112887	A2	10/2006
WO	2007001294	A1	1/2007
WO	2007013889	A2	2/2007
WO	2007024241	A2	3/2007
WO	2007024323	A2	3/2007
WO	2007019439	A3	5/2007
WO	2007055041	A1	5/2007
WO	2008055137	A2	5/2008
WO	2008091741	A2	7/2008
WO	2008096335	A2	8/2008
WO	2008097736	A2	8/2008
WO	2008118635	A2	10/2008
WO	2008124219	A2	10/2008
WO	2008130847	A1	10/2008
WO	2008145268	A1	12/2008
WO	2008156977	A2	12/2008
WO	2009099924	A2	8/2009
WO	2009102551	A2	8/2009
WO	2009117238	A2	9/2009
WO	2009117243	A1	9/2009
WO	2009134635	A2	11/2009

OTHER PUBLICATIONS

Melde et al., Silica Nanostructures Templated by Oriented Block Copolymer Thin Films Using Pore-Filling and Selective-Mineralization Routes, Chem. Mater., vol. 17, No. 18, Aug. 13, 2005, pp. 4743-4749.

La, Young-Hye, et al., "Directed Assembly of Cylinder-Forming Block Copolymers into Patterned Structures to Fabricate Arrays of Spherical Domains and Nanoparticles," Chem. Mater, 2007, vol. 19, No. 18, Department of Chemical and Biological Engineering and Center for Nanotechnology, Univ. of Wisconsin, pp. 4538-4544.

La, Young-Hye, et al., "Pixelated Chemically Amplified Resists: Investigation of Material Structure on the Spatial Distribution of Photoacids and Line Edge Roughness," J. Vac. Sci. Technol. B 25(6), Nov./Dec. 2007, American Vacuum Society, pp. 2508-2513.

Laracuente, A.R., et al., "Step Structure and Surface Morphology of Hydrogen-terminated Silicon: (001) to (114)," Surface Science 545, 2003, pp. 70-84.

Lentz, D, et al., "Whole Wafer Imprint Patterning Using Step and Flash Imprint Lithography: A Manufacturing Solution for Sub 100 nm Patterning", SPIE Advanced Lithography Paper, http://molecularimprints.com/NewsEvents/tech_articles/new_articles/SPIE_07_MII_WW_Paper.pdf), Molecular Imprints, Inc., Texas, USA, Feb. 2007, pp. 1-10.

Li, Mingqi, et al., "Block Copolymer Patterns and Templates," Materials Today, vol. 9, No. 9, Sep. 2006, pp. 30-39.

Li, Wai-Kin, et al, "Creation of Sub-20-nm Contact Using Diblock Copolymer on a 300 mm Wafer for Complementary Metal Oxide Semiconductor Applications," J. Vac. Sci. Technol. B 25(6), Nov./Dec. 2007, American Vacuum Society, pp. 1982-1984.

Li, Xue, et al., "Morphology Change of Asymmetric Diblock Copolymer Micellar Films During Solvent Annealing," ScienceDirect, Polymer 48 (2007), pp. 2434-2443.

Li, Yong, et al., "A Method for Patterning Multiple Types of Cells by Using Electrochemical Desorption of Self-Assembled Monolayers within Microfluidic Channels," Angew. Chem. Int. Ed., vol. 46, pp. 1094-1096, 2007.

Lin, Zhiqun, et al., "A Rapid Route to Arrays of Nanostructures in Thin Films," Adv. Mater. 2002, 14 No. 19, Oct. 2, pp. 1373-1376.

Lin-Gibson, Sheng, et al., "Structure-Property Relationships of Photopolymerizable Poly(ethylene glycol)Dimethacrylate Hydrogels," Macromolecules 2005, 38, American Chemical Society, pp. 2897-2902.

(56) **References Cited**

OTHER PUBLICATIONS

Liu et al., Pattern Transfer Using Poly(styrene-block-methyl methacrylate) Copolymer Films and Reactive Ion Etching, J. Vac. Sci. Technol. B vol. 25, No. 6, Nov./Dec. 2007, pp. 1963-1968.
Loo et al., "Additive, nanoscale patterning of metal films with a stamp and a surface chemistry mediated transfer process: Applications in plastic electronics," Applied Physics Letters, vol. 81, No. 3, Jul. 15, 2002, pp. 562-564.
Lopes et al., Hierarchical Self-Assembly of Metal Nanostructures on Diblock Copolymer Scaffolds, Nature, vol. 414, Dec. 13, 2001, pp. 735-738.
Lutolf, M., et al., "Cell-Responsive Synthetic Hydrogels," Adv. Mater., vol. 15, No. 11, Jun. 2003, pp. 888-892.
Lutolf, M.P., et al, "Synthetic Biomaterials as Instructive Extracellular Microenvironments for Morphogenesis in Tissue Engineering," Nature Biotechnology, 23, 47-55 (2005), Abstract only.
Lutz, Jean-Francois, "1,3-Dipolar Cycloadditions of Azides and Alkynes: A Universal Ligation Tool in Polymer and Materials Science," Angew. Chem. Int. Ed., vol. 46, pp. 1018-1025, 2007.
Malenfant et al., Self-Assembly of an Organic-Inorganic Block Copolymer for Nano-Ordered Ceramics, Nature Nanotechnology, vol. 2, pp. 43-46 (2007).
Malkoch, M., et al., "Synthesis of Well-defined Hydrogel Networks Using Click Chemistry," Chem. Commun., 2006, The Royal Society of Chemistry, pp. 2774-2776.
Mansky, P., et al., "Controlling Polymer-Surface Interactions with Random Copolymer Brushes," Science, vol. 275, Mar. 7, 1997, pp. 1458-1460.
Martens, P., et al., "Characterization of Hydrogels Formed from Acrylate Modified Poly(vinyl alcohol) Macromers," Polymer, vol. 41, Issue 21, Oct. 2000, pp. 7715-7722, Abstract only.
Matsuda, T., et al., "Photoinduced Prevention of Tissue Adhesion," ASAIO J, Jul.-Sep. 1992; 38(3): M154-7, Abstract only.
Maye, M. A., et al., "Chemical Analysis Using Force Microscopy," Journal of Chemical Education, vol. 79, No. 2, Feb. 2002, Dept. of Chemistry, State Univ. of New York at Binghamton, USA, pp. 207-210.
Metters, A., et al., "Network Formation and Degradation Behavior of Hydrogels Formed by Michael-Type Addition Reactions," Biomacromolecules 2005, 6, 2005, pp. 290-301.
Meyer, E., et al., "Controlled Dewetting Processes on Microstructured Surfaces—a New Procedure for Thin Film Microstructuring," Macromollecular Mater. Eng., 276/277, 2000, Institute of Polymer Research Dresden, pp. 44-50.
Mezzenga, R., et al., "On the Role of Block Copolymers in Self-Assembly of Dense Colloidal Polymeric Systems," Langmuir 2003, vol. 19, No. 20, 2003, American Chemical Society, pp. 8144-8147.
Mindel, J., et.al., "A Study of Bredig Platinum Sols", The Chemical Laboratories of New York University, received Jun. 10, 1943, vol. 65 pp. 2112.
Naito, K., et al., "2.5-Inch Disk Patterned Media Prepared by an Artificially Assisted Self-Assembling Method," IEEE Transactions on Magnetics, vol. 38, No. 5, Sep. 2002, pp. 1949-1951.
Nealey, P. F., et al., "Self-Assembling Resists for Nanolithography", IProceedings of the IEEE International Electron Devices Meeting, IEDM Technical Digest, 356-359 (2005).
Nguyen, K. T., et al., "Photopolymerizable Hydrogels for Tissue Engineering Applications," Biomaterials 23, 2002, pp. 4307-4314.
Nishikubo, T., "Chemical Modification of Polymers via a Phase-Transfer Catalyst or Organic Strong Base," American Chemical Society Symposium Series, 1997, American Chemical Society, pp. 214-230.
Niu, Sanjun, et al., "Stability of Order in Solvent-Annealed Block Copolymer Thin Films," Macromolecules, vol. 36, No. 7, 2003, Univ. of Nebraska, USA, pp. 2428-2440, (web release date: Mar. 13, 2003) (http://digitalcommons.uni.edu/cgi/viewcontent.cgi?article+1005 &contect=chemeng_nanotechnology).
Niu, Sanjun, et al., "Selective assembly of nanoparticles on block copolymer by surface modification," Nanotechnology, vol. 18, pp. 1-4, 2007.
Olayo-Valles, R., et al., "Large Area Nanolithographic Templates by Selective Etching of Chemically Stained Block Copolymer Thin Films," J. Mater. Chem, 2004, 14, The Royal Society of Chemistry, pp. 2729-2731.
Parejo, P. G., et al., "Highly Efficient UV-absorbing Thin-film Coatings for Protection of Organic Materials Against Photodegradation," J. Mater. Chem, 2006, 16, The Royal Society of Chemistry, pp. 2165-2169.
Park et al., Fabrication of Highly Ordered Silicon Oxide Dots and Stripes from Block Copolymer Thin Films, Advanced Materials, vol. 20, pp. 681-685, 2008.
Park et al., High-Aspect-Ratio Cylindrical Nanopore Arrays and Their Use for Templating Titania Nanoposts, Advanced Materials, vol. 20, pp. 738-742, 2008.
Park, Cheolmin, et al., "Enabling Nanotechnology with Self Assembled Block Copolymer Patterns," Polymer 44, 2003, pp. 6725-6760.
Park, Dae-Ho, "The Fabrication of Thin Films with Nanopores and Nanogrooves from Block Copolymer Thin Films on the Neutral Surface of Self-assembled Monolayers," Nanotechnology 18, 2007, 355304, IIOP Publishing LTD, UK, pp. 1-7.
Park, M., et al., "Block Copolymer Lithography: Periodic Arrays of 1011 Holes in 1 Square Centimeter," Science, vol. 276, No. 5317, May 30, 1997, pp. 1401-1404.
Park, Sang-Min, et al., "Directed assembly of lamellae-forming block copolymers using chemically and topographically patterned substrates," Advanced Materials, vol. 19, No. 4, pp. 607-611, Feb. 2007.
Park, Seung Hak, et al., "Block Copolymer Multiple Patterning Integrated with Conventional ArF Lithography," Soft Matter, 2010, 6, Royal Society of chemistry, pp. 120-125.
Park, Sung Chan, et al., "Controlled Ordering of Block Copolymer Thin Films by the Addition of Hydrophilic Nanoparticles," Macromolecules 2007, vol. 40, No. 22, American Chemical Society, pp. 8119-8124.
Peng, J., et. al., "Development of Nanodomain and Fractal Morphologies in Solvent Annealed Block copolymer Thin Films," Macromol. Rapid Commun. 2007, 28, pp. 1422-1428.
Peters, R. D., et al., "Combining Advanced Lithographic Techniques and Self-assembly of Thin Films of Diblock Copolymers to Produce Templates for Nanofabrication," J. Vac. Sci. Technol. B, vol. 18, No. 6, Nov./Dec. 2000, American Vacuum Society, pp. 3530-3532.
Peters, R. D., et al., "Morphology of Thin Films of Diblock Copolymers on Surfaces Micropatterned with Regions of Different Interfacial Energy," Macromolecules, vol. 35, No. 5, 2002, American Chemical Society, pp. 1822-1834.
Potemkin, Igor I., et al., "Effect of the Molecular Weight of AB Diblock Copolymers on the Lamellar Orientation in Thin Films: Theory and Experiment," Macromol. Rapid Commun., 2007, 28, pp. 579-584.
Reed, M.A., et al., "Molecular random access memory cell," Appl. Phys. Lett., vol. 78, No. 23, pp. 3735-3737, Jun. 2001.
Resnick, D. J., et al., "Initial Study of the Fabrication of Step and Flash Imprint Lithography Templates for the Printing of Contact Holes," Microlith., Microfab., Microsyst., vol. 3, No. 2, Apr. 2004, Society of Photo-Optical Instrumentation Engineers, pp. 316-321.
Rogers, J. A., "Slice and Dice, Peel and Stick: Emerging Methods for Nanostructure Fabrication," ACS Nano, vol. 1, No. 3, 2007, pp. 151-153.
Rozkiewicz, Dorota I., et al., "'Click' Chemistry by Microcontact Printing," Angew. Chem. Int. Ed., vol. 45, pp. 5292-5296, 2006.
Electronegativity—<http://www.princeton.edu/~achaney/tmve/wiki100k/docs/Electronegativity.html> website, visited Aug. 28, 2013, 1 page.
Zhou et al., Nanoscale Metal/Self-Assembled Monolayer/Metal Heterostructures, American Institute of Physics, pp. 611-613 (1997).
Zhu, X. Y., et al., "Molecular Assemblies on Silicon Surfaces via Si—O Linkages," Langmuir, vol. 16, 2000, American Chemical Society, pp. 6766-6772.
Zhu, X.Y., et al., "Grafting of High-Density Poly(Ethylene Glycol) Monolayers on Si(111)," Langmuir, vol. 17, pp. 7798-7803, 2001.
Chang et al., Experimental Demonstration of Aperiodic Patterns of Directed Self-Assembly by Block Copolymer Lithography for Ran-

(56) **References Cited**

OTHER PUBLICATIONS

dom Logic Circuit Layout, Electron Devices Meeting (IEDM), 2010 IEEE International, Dec. 6-8, 2010, pp. 33.2.1-33.2.4.
Tang et al., Evolution of Block Copolymer Lithography to Highly Ordered Square Arrays, Science, vol. 322, No. 5900, Sep. 25, 2008, pp. 429-432.
Tseng et al., Enhanced Block Copolymer Lithography Using Sequential Infiltration Synthesis, The Journal of Physical Chemistry, vol. 115, No. 36, Sep. 15, 2011, 15 pages.
Ali, H. A., et al., Properties of Self-assembled ZnO Nanostructures, Solid-State Electronics 46 (2002), 1639-1642.
Arshady, R., et al., "The Introduction of Chloromethyl Groups into Styrene-based Polymers, 1," Makromol. Chem., vol. 177, 1976, p. 2911-2918.
Asakawa et al., Fabrication of Subwavelength Structure for Improvement in Light-Extraction Efficiency of Light-Emitting Devices Using a Self-Assembled Pattern of Block Copolymer, http://www.research.ibm.com/journal/rd/515/black.html, IBM Journal of Research and Development, vol. 51, No. 5, 2007.
Bae, Joonwon, "Surface Modification Using Photo-Crosslinkable Random Copolymers", Abstract submitted for the Mar. 2006 meeting of The American Physical Society, submitted Nov. 30, 2005. (Accessed via the Internet [retrieved on Apr. 5, 2000], URL: http://absimage.aps.org/image/MWS_MAR06-2005-003641.pdf).
Balsara, C., et al, CPIMA, IRG Technical Programs, Synthesis and application of Nanostructured Materials, Leland Stanford Junior Univ., 2006, http://www.stanford.edu/group/cpima/irg/irg_1.htm, printed Jul. 1, 2009.
Bang, J., "The Effect of Humidity on the Ordering of Tri-block Copolymer Thin Films," Abstract submitted for the Mar. 2007 meeting of The American Physical Society, submitted Nov. 20, 2006.
Bass, R. B., et al., "Microcontact Printing with Octadecanethiol", Applied Surface Science, 226(4), pp. 335-340, Apr. 2004, http://www.ece.virginia.edu/UVML/sis/Papers/rbbpapers/assoct.pdf.
Bearinger, J. P., et al., "Chemisorbed Poly(propylene sulphide)-based Copolymers Resist Biomolecular Interactions," Nature Materials 2, 259-264, 2003, (published online Mar. 23, 2003). Published online Mar. 23, 2003.
Berry, B. C., et al., "Orientational Order in Block Copolymer Films Zone Annealed Below the Order-Disorder Transition Temperature," Nano Letters vol. 7, No. 9 Aug. 2007, Polymers Division, Nat'l. Inst. of Standards and Technology, Maryland, USA, pp. 2789-2794, (published on Web Aug. 11, 2007).
Berry, B. C., et al., "Effects of Zone Annealing on Thin Films of Block Copolymers", National Institute of Standard and Technology, Polymers Division, Maryland, USA, 2007, 2 pages.
Black et al., Integration of Self-Assembled Diblock Copolymers for Semiconductor Capacitor Fabrication, Applied Physics Letters, vol. 79, No. 3, pp. 409-411 (2001).
Black et al., Polymer Self Assembly in Semiconductor Microelectronics, IBM J. Res. & Dev. vol. 51, No. 5, Sep. 2007, pp. 605-633.
Black, C .T. et al., "Integration of Self Assembly for Semiconductor Microelectronics," IEEE 2005 Custom Integrated Circuits Conference, IBM T.J. Watson Research Center, pp. 87-91.
Black, C. T., "Self-aligned self-assembly of multi-nanowire silicon field effect transistors," Appl. Phys. Lett, vol. 87, pp. 163116-1 through 163116-3, 2005.
Black, C. T., "Polymer Self-Assembly as a Novel Extension to Optical Lithography," ACSNano, vol. 1, No. 3, 2007, American Chemical Society, pp. 147-150.
Black, C. T., et al., "High-Capacity, Self-Assembled Metal-Oxide-Semiconductor Decoupling Capacitors," IEEE Electron Device Letters, vol. 25, No. 9, Sep. 2004, pp. 622-624.
Black, C. T., et al., "Nanometer-Scale Pattern Registration and Alignment by Directed Diblock Copolymer Self-Assembly," IEEE Transactions on Nanotechnology, vol. 3, No. 3, pp. 412-415, Sep. 2004.
Black, C. T., et al., "Self Assembly in Semiconductor Microelectronics: Self-Aligned Sub-Lithographic Patterning Using Diblock Copolymer Thin Films," Proc. of SPIE, vol. 6153, 615302 (2006).
Black, C. T., et al., Polymer Self Assembly in Semiconductor Microelectronics, IBM J. Res. & Dev. vol. 51, No. 5, Sep. 2007, pp. 605-633.
Botelho Do Rego, A. M, et al., "Diblock Copolymer Ultrathin Films Studied by High Resolution Electron Energy Loss Spectroscopy," Surface Science, 482-485 (2001), pp. 1228-1234.
Brydson, R. M., et al. (chapter authors), "Generic Methodologies for Nanotechnology: Classification and Fabrication", Nanoscale Science and Technology, edited by R.W. Kelsall, et al., 2005 John Wiley & Sons, Ltd., (published online: Dec. 20, 2005) (http://www3.interscience.wiley.com/cgi-bin/summary/112217550/SUMMARY).
Bulpitt, P., et al, "New Strategy for Chemical Modification of Hyaluronic Acid: Preparation of Functionalized Derivatives and Their Use in the Formation of Novel Biocompatible Hydrogels," Journal of Biomedical Materials Research, vol. 47, Issue 2, pp. 152-169, Published online Aug. 13, 1999, Abstract only.
Canaria, C. A., et al., "Formation and Removal of Alkylthiolate Self-Assembled Monolayers on Gold in Aqueous Solutions", Lab Chip 6, 289-295 (2006), http://www.rsc.org/publishing/journals/LC/article.asp?doi=b51066c) (Abstract).
Candau, F., et al., "Synthesis and Characterization of Polystyrene-poly(ethylene oxide) Graft Copolymers," Polymer, 1977, vol. 18, pp. 1253-1257.
Cavicchi, K. A., et al., "Solvent Annealed Thin Films of Asymmetric Polyisoprene-Polylactide Diblock Copolymers," Macromolecules 2007, vol. 40, 2007, Univ. of Massachusetts, pp. 1181-1186.
Cha, J. N., et al., Biomimetic Approaches for Fabricating High-Density Nanopatterned Arrays, Chem. Mater. vol. 19, 2007, pp. 839-843.
Chai et al., Assembly of Aligned Linear Metallic Patterns on Silicon, Nature Nanotechnology, Vol, 2, Aug. 2007, pp. 500-506.
Chai et al., Using Cylindrical Domains of Block Copolymers to Self-Assemble and Align Metallic Nanowires, American Chemical Society, www.Acsnano.org, 2008. pp. A-K.
Chandekar, A., et al., "Template-Directed Adsorption of block Copolymers on Alkanethiol-Patterned Gold Surfaces," (circa 2006), http://www.nano.neu.edu/industry/industry_showcase/industry_day/documents/Chandekar.pdf) (Powerpoint template for scientific posters (Swarthmore College)).
Chang, Li-Wen, "Diblock Copolymer Directed Self-Assembly for CMOS Device Fabrication," Proc. of SPIE, vol. 6156, 2006, 615611-1 to 615611-6.
Chen et al., Highly Ordered Arrays of Mesoporous Silica Nanorods with Tunable Aspect Ratios from Block Copolymer Thin Films, Advanced Materials, vol. 20, pp. 763-767, 2008.
Cheng, J. Y., et al., "Rapid Directed Self Assembly of Lamellar Microdomains from a Block Copolymer Containing Hybrid," Applied Physics Letters, 91, 143106-143106-3 (2007).
Cheng, J. Y., et al., "Self-Assembled One-Dimensional Nanostructure Arrays," Nano Letters, vol. 6, No. 9, 2006, pp. 2099-2103.
Cheng, J. Y., et al., "Templated Self-Assembly of Block Copolymers: Effect of Substrate Topography," Adv. Mater. 2003, vol. 15, No. 19, pp. 1599-1602.
Cho et al., Nanoporous Block Copolymer Micelle/Micelle Multilayer Films with Dual Optical Properties, J. Am. Chem. Soc., vol. 128, No. 30, pp. 9935-9942 (2006).
Choi, H. J., et al., "Magnetorheology of Synthesized Core-Shell Structured Nanoparticle," IEEE Transactions on Magnetics, vol. 41, No. 10, Oct. 2005, pp. 3448-3450.
Clark et al., "Selective Deposition in Multilayer Assembly: SAMs as Molecular Templates," Supramolecular Science, vol. 4, pp. 141-146, (1997).
Daoulas Kostas CH., et al., "Fabrication of Complex Three-Dimensional Nanostructures from Self-Assembling Block Copolymer Materials on Two-Dimensional Chemically Patterned Templates with Mismatched Symmetry," Physical Review Letters 96, week ending Jan. 27, 2006, pp. 036104-1-036104-3.
Darling, S. B., "Directing the Self-assembly of Block Copolymers," Progress in Polymer Science, vol. 32, No. 10, Sep. 28, 2007, pp. 1152-1204.

(56) **References Cited**

OTHER PUBLICATIONS

Desai, Dr. Trejal A., et al., "Engineered Silicon Surfaces for Biomimetic Interfaces," Business Briefing: Medical Device Manufacturing & Technology, 2002.
Edwards, E. W., et al., "Mechanism and Kinetics of Ordering in Diblock Copolymer Thin Films on Chemically Nanopatterned Substrates," Journal of Polymer Science: Part B Polymer Physics, vol. 43, 3444-3459, 2005.
Edwards, E. W., et al., "Precise Control over Molecular Dimensions of Block-Copolymer Domains Using the Interfacial Energy of Chemically Nanopatterned Substrates," Advanced Mater., 16, No. 15, Aug. 4, 2004, pp. 1315-1319.
Elisseeff, J., et al., "Photoencapsulation of Chondrocytes in Poly(ethylene oxide)-based Semi-interpenetrating Networks," Journal of Biomedical Materials Research, 51(2): 164-171, Aug. 2000, Abstract only.
Erlandsson, Mikael, et al., "Metallic Zinc Reduction of Disulfide Bonds between Cysteine Residues in Peptides and Proteins," International Journal of Peptide Research and Therapeutics, vol. 11, No. 4, pp. 261-265, Dec. 2005.
Fasolka et al., Block Copolymer Thin Films: Physics and Applications, Annual Review, vol. 31, pp. 323-355 (2001).
Fasolka, M. J. et al., "Morphology of Ultrathin Supported Diblock Copolymer Films: Theory and Experiment," Macromolecules 2000, vol. 33, No. 15, pp. 5702-5712.
Fukunaga, K., et al., "Self-Assembly of Block Copolymer Thin Films Having a Half-Domain-Spacing Thickness: Nonequilibrium Pathways to Achieve Equilibrium Brush Layers Parallel to Substrate," Macromolecules vol. 39, Aug. 2006, pp. 6171-6179.
Gates, "Nanofabrication with Molds and Stamps," Materials Today, pp. 44-49, (Feb. 2005).
Gates, B. D., et al., "Unconventional Nanofabrication," Annu. Rev. Mater. Res. 2004, 34:339-72.
Ge, Zhenbin, et al., "Thermal Conductance of Hydrophilic and Hydrophobic Interfaces," PRL 96, 186101-1-186101-4, The American Physical Society, week ending May 12, 2006.
Gelest Inc., "Silane Coupling Agents: Connecting Across Boundaries," v2.0, 2006, pp. 1-56.
Genua, A., et al., "Functional Patterns Obtained by Nanoimprinting Lithography and Subsequent Growth of Polymer Brushes," Nanotechnology, 18, (2007), IOP Publishing Ltd., pp. 1-7.
Gillmor, S. D., et al., "Hydrophilic/Hydrophobic Patterned Surfaces as Templates for DNA Arrays," Langmuir 2000, vol. 16, No. 18, 2000, pp. 7223-7228.
Grubbs, Hybrid Metal-Polymer Composites from Functional Block Copolymers, Journal of Polymer Science: Part A: Polymer Chemistry, vol. 43, pp. 4323-4336 (2005).
Guarini et al., Nanoscale Patterning Using Self-Assembled Polymers for Semiconductor Applications, J. Vac. Sci. Technol. B 19(6), pp. 2784-2788, Nov./Dec. (2001).
Gudipati, C. S., et al., "Hyperbranched Fluoropolymer and Linear Poly(ethylene glycol) Based Amphiphilic Crosslinked Networks as Efficient Antifouling Coatings: An Insight into the Surface Compositions, Topographies, and Morphologies," Journal of Polymer Science Part A: Polymer Chemistry, vol. 42, (2004), pp. 6193-6208.
Guo, Kai, et al., Abstract of "Synthesis and Characterization of Novel Biodegradable Unsaturated Poly(ester amide)/Poly(ethylene glycol) Diacrylate Hydrogels", Journal of Polymer Science Part A: Polymer Chemistry, vol. 43, Issue 17, 2005 Wiley Periodicals, Inc., pp. 3932-3944.
Hadziioannou, Semiconductor Block Copolymers for Self-Assembled Photovoltaic Devices, MRS Bulletin, pp. 456-460 (2002).
Hamers, Robert J., "Passivation and activation: How do monovalent atoms modify the reactivity of silicon surfaces? A perspective on the article, 'The mechanism of amine formation on Si(100) activated with chlorine atoms,'" Surface Science, vol. 600, pp. 3361-3362, 2006.
Hamley, I. W., "Introduction to Block Copolymers", Developments in Block Copolymers Science and Technology, John Wiley & Sons, Ltd., 2004, pp. 1-29.
Hammond, M. R., et al., "Temperature Dependence of Order, Disorder, and Defects in Laterally Confined Diblock Copolymer Cylinder Monolayers," Macromolecules, vol. 38, Jul. 2005; American Chemical Society, p. 6575-6585.
Harrison, C., et al., "Layer by Layer Imaging of Diblock Copolymer Films with a Scanning Electron Microscope," Polymer, vol. 39, No. 13, 1998, pp. 2733-2744.
Hawker, C. J., et al., "Facile Synthesis of Block Copolymers for Nanolithographic Applications," Polymer Reprints, American Chemical Society (2005).
Hawker, C. J., et al., Abstract for "Improving the Manufacturability and Structural Control of Block Copolymer Lithography," Abstracts of Papers, 232nd ACS National Meeting, San Francisco, CA, Sep. 10-14, 2006.
Hayward et al., Crosslinked Poly(styrene)-block-Poly(2-vinylpyridine) Thin Films as Swellable Templates for Mesostructured Silica and Titania, Advanced Materials, vol. 17, 2005, pp. 2591-2595.
He et al., "Self-Assembly of Block Copolymer Micelles in an Ionic Liquid," J. Am. Chem. Soc. 2006, 128, pp. 2745-2750.
Helmbold, A., et al., "Optical Absorption of Amorphous Hydrogenated Carbon Thin Films," Thin Solid Films 283 (1996) pp. 196-203.
Helmuth, Jo A., et al., "High-Speed Microcontact Printing," J. Am. Chem. Soc., vol. 128, No. 29, pp. 9296-9297, 2006.
Hermans, T. M., et al., "Application of Solvent-Directed Assembly of Block Copolymers to the Synthesis of Nanostructured Materials with Low Dielectric Constants", Angewandte Chem. Int. Ed., vol. 45, Issue 40, Oct. 13, 2006, pp. 6648-6652.
Horiuchi et al., Three-Dimensional Nanoscale Alignment of Metal Nanoparticles Using Block Copolymer Films as Nanoreactors, Langmuir, vol. 19, pp. 2963-2973 (2003).
Huang et al., "Stretchable gold conductors on elastomeric substrates," Applied Physics Letters, vol. 82, No. 15, p. 2404.
Huang et al., "Using Surface Active Random Copolymers to Control the Domain Orientation in Diblock Copolymer Thin Films," Macromolecules, 1998, 31, 7641-7650.
Hur et al., "Nanotransfer printing by use of noncovalent surface forces: Applications to thin-film transistors that use single-walled carbon nanotube networks and semiconducting polymers," Applied Physics Letters, vol. 85, No. 23, Dec. 6, 2004, pp. 5730-5732.
Hutchison, J. B, et al., "Polymerizable Living Free Radical Initiators as a Platform to Synthesize Functional Networks," Chem. Mater., vol. 17, No. 19, 2005, pp. 4789-4797.
Ikeda, Susumu, et al., "Control of Orientation of Thin Films of Organic Semiconductors by Graphoepitaxy," NanotechJapan Bulletin—vol. 3, No. 3, Dec. 17, 2010/Focus 26-06, NIMS International Center for Nanotechnology Network.
In, Insik, et al., "Side-Chain-Grafted Random Copolymer Brushes as Neutral Surfaces for Controlling the Orientation of Block Copolymer Microdomains in Thin Films," Langmuir, vol. 22, No. 18, 2006, Department of Materials Science and Engineering and Chemical and Biological Engineering, Univ. of Wisconsin-Madison, pp. 7855-7860.
Ji, Shengxiang, et al., "Generalization of the Use of Random Copolymers to Control the Wetting Behaviors of Block Copolymer Films," Macromolecules, 2008, 41(23): 9098-9103.
Ji, Shengxiang, et al., "Molecular Transfer Printing Using Block Copolymers," ACS Nano, vol. 4, No. 2, 2010, Dept. of Chemical and Biological Engineering, Univ. of Wisconsin, pp. 599-609.
Ji, Shengxiang, et al., "Preparation of Neutral Wetting Brushes for Block Copolymer Films from Homopolymer Blends," submitted to Advanced Materials, 20(16): 3054-3060; published online Jul. 7, 2008.
Jiang, Xingyu, et al., "Electrochemical Desorption of Self-Assembled Monolayers Noninvasively Releases Patterned Cells from Geometrical Confinements," J. Am. Chem. Soc., vol. 125, No. 9, pp. 2366-2367, 2003.
Johnson, Daniel L., et al., "Probing the stability of the disulfide radical intermediate of thioredoxin using direct electrochemistry," Letters in Peptide Science, vol. 10, pp. 495-500, 2003.
Jun, Y., et al., "Microcontact Printing Directly on the Silicon Surface," Langmuir, 2002, 18(9), pp. 3415-3417, Abstract only.

(56) **References Cited**

OTHER PUBLICATIONS

Jun, Yongseok, et al., "Microcontact Printing Directly on the Silicon Surface," Langmuir, vol. 18, No. 9, pp. 3415-3417, 2002.
Jun, Yongseok, et al., "Patterning protein molecules on poly(ethylene glycol) coated Si(111)," Biomaterials, vol. 25, pp. 3503-3509, 2004.
Karim, Alamgir, et al., "Control of Ordering Kinetics and Morphology Using Zone Annealing of Thin Block Copolymer Films", Abstract submitted for the Mar. 2007 Meeting of the American Physical Society, Nov. 20, 2006.
Kavakli et al., Single and Double-Layer Antireflection Coatings on Silicon, Turk J Phys, vol. 26, pp. 349-354 (2002).
Kim, Is, et al., "Self-assembled Hydrogel Nanoparticles Composed of Dextran and Poly (ethylene glycol) Macromer," Int J Pharm., Sep. 15, 2000; 205(1-2): 109-116, Abstract only.
Kim, Sang Ouk, et al., "Epitaxial Self-assembly of Block Copolymers on Lithographically Defined Nanopatterned Substrates," Nature, vol. 424, Jul. 24, 2003, Dept. of Chemical Engineering and Center for Nanotechnology, and Dept. of Mechanical Engineering, Univ. of Wisconsin, pp. 411-414.
Kim, Sang Ouk, et al., "Novel Complex Nanostructure from Directed Assembly of Block Copolymers on Incommensurate Surface Patterns," Adv. Mater., 2007, 19, pp. 3271-3275.
Kim, Seung Hyun, et al., "Highly Oriented and Ordered Arrays from Block Copolymers via Solvent Evaporation," Adv. Mater. 2004, 16, No. 3, Feb. 3, pp. 226-231.
Kim, Seung Hyun, et al., "Salt Complexation in Block Copolymer Thin Films," Macromolecules 2006, vol. 39, No. 24, 2006, pp. 8473-8479.
Kim, Seung Hyun, et al., "Solvent-Induced Ordering in Thin Film Diblock Copolymer/Homopolymer Mixtures," Advanced Mater., vol. 16, No. 23-24, Dec. 17, 2004, pp. 2119-2123.
Kim, SH, et al., "In Vitro Release Behavior of Dextran-methacrylate Hydrogels Using Doxorubicin and Other Model Compounds," J Biomater Appl., Jul. 2000; 15(1): 23-46 Abstract only.
Kim, SH, et al., "Synthesis and characterization of Dextran-methacrylate Hydrogels and Structural Study by SEM," J . Biomater Res., Mar. 15, 2000; 49(4): 517-27 Abstract only.
Kim, Su-Jin, et al., "Hybrid Nanofabrication Processes Utilizing Diblock Copolymer Nanotemplate Prepared by Self-assembled Monolayer Based Surface Neutralization," J. Vac. Sci. Technol. B26(1), Jan./Feb. 2008, © 2008 American Vacuum Society, pp. 189-194.
Knoll, A., et al., "Phase Behavior in Thin Films of Cylinder-Forming Block Copolymers," Physical Review Letters vol. 89, No. 3 Jul. 2002, The American Physical Society, pp. 035501-1 to 035501-4.
Krishnamoorthy et al., Block Copolymer Micelles as Switchable Templates for Nanofabrication, Languir, vol. 22, No. 8, Mar. 17, 2006, pp. 3450-3452.
Krishnamoorthy et al., Nonopatterned Self-Assembled Monolayers by Using Diblock Copolymer Micelles as nanometer-Scale Adsorption and Etch Masks, Advanced Materials, 2008, pp. 1-4.
Krishnamoorthy, S., et al., "Nanoscale Patterning with Block Copolymers," Materials Today, vol. 9, No. 9, Sep. 2006, pp. 40-47.
Kuhnline et al., "Detecting thiols in a microchip device using micromolded carbon ink electrodes modified with cobalt phthalocyanine", Analyst, vol. 131, pp. 202-207, (2006).
Ruiz, R., et al., "Density Multiplication and Improved Lighography by Directed Block Copolymer Assembly," Science, vol. 321, Aug. 15, 2008, pp. 936-939.
Ruiz, R., et al., "Induced Orientational Order in Symmetric Diblock Copolymer Thin-Films," Advanced Materials, vol. 19, No. 4, pp. 587-591, (2007).
Ryu, Du Yeol, et al., "Surface Modification with Cross-Linked Random Copolymers: Minimum Effective Thickness," Macromolecules, vol. 40, No. 12, 2007, American Chemical Society, pp. 4296-4300.
Sang et al., "Epitaxial self-assembly of block copolymers on lithographically defined nanopatterned substrates", Nature, vol. 24, pp. 411-414, (Jul. 2003).
Saraf, Ravi R., et al., "Spontaneous Planarization of Nanoscale Phase Separated Thin Film," Applied Physics Letters, vol. 80, No. 23, Jun. 10, 2002, American Institute of Physics, pp. 4425-4427.
Sato et al., Novel Antireflective Layer Using Polysilane for Deep Ultraviolet Lithography, J. Vac. Sci. Technol. B, vol. 17, No. 6, pp. 3398-3401 (1999).
Sawhney, A. S., et al., "Bioerodible Hydrogels Based on Photopolymerized Poly(ethylene glycol)-co-poly(a-hydroxy acid) Diacrylate Macromers," Macromolecules 1993, 26, American Chemical Society, pp. 581-587, Abstract only.
Segalman, R. A., "Patterning with Block Copolymer Thin Films," Materials Science and Engineering R 48 (2005), Elsevier B. V., pp. 191-226.
Shahrjerdi, D., et al., "Fabrication of Ni Nanocrystal Flash Memories Using a Polymeric Self-Assembly Approach," IEEE Electron Device Letters, vol. 28, No. 9, Sep. 2007, pp. 793-796.
Sharma, S. et al., "Ultrathin Poly(ethylene glycol) Films for Silicon-based Microdevices," Applied Surface Science, 206 (2003), Elsevier Science B.V., pp. 218-229.
Sigma-Aldrich, 312-315Tutorial regarding Materials for Lithography/Nanopatterning, http://www.sigmaaldrich.com/Area_of_Interest/Chemistry/Materials_Science/Micro_and_Nanoelectronic website, retrieved Aug. 27, 2007.
Sivaniah, E., et al., "Observation of Perpendicular Orientation in Symmetric Diblock Copolymer Thin Films on Rough Substrates," Macromolecules 2003, 36, American Chemical Society, pp. 5894-5896.
Sivaniah, et al., "Symmetric Diblock Copolymer Thin Films on Rough Substrates, Kinetics and Structure Formation in Pure Block Copolymer Thin Films," Macromolecules 2005, 38, American Chemical Society, pp. 1837-1849.
Sohn et al., Fabrication of the Multilayered Nanostructure of Alternating Polymers and Gold Nanoparticles with Thin Films of Self-Assembling Diblock Copolymers, Chem, Mater, vol. 13, pp. 1752-1757 (2001).
Solak, H. H., "Nanolithography with Coherent Extreme Ultraviolet Light," Journal of Physics D: Applied Physics, 2006, IOP Publishing Ltd., UK, pp. R171-188.
Srinvivasan, C., et al., "Scanning Electron Microscopy of Nanoscale Chemical Patterns," ACS Nano, vol. 1, No. 3, pp. 191-201, 2007.
Stoykovich, M. P., et al., "Directed Assembly of Block Copolymer Blends into Nonregular Device-Oriented Structures," Science, vol. 308, Jun. 3, 2005, pp. 1442-1446.
Stoykovich, M. P., et al., "Directed Self-Assembly of Block Copolymers for Nanolithography: Fabrication of Isolated Features and Essential Integrated Circuit Geometries," ACS Nano, vol. 1, No. 3, 2007, pp. 168-175.
Sundrani, D., et al., "Guiding Polymers to Perfection: Macroscopic Alignment of Nanoscale Domains," Nano Lett., vol. 4, No. 2, 2004, American Chemical Society, pp. 273-276.
Sundrani, D., et al., "Hierarchical Assembly and Compliance of Aligned Nanoscale Polymer Cylinders in Confinement," Langmuir 2004, vol. 20, No. 12, 2004, American Chemical Society, pp. 5091-5099.
Tadd et al, Spatial Distribution of Cobalt Nanoclusters in Block Copolymers, Langmuir, vol. 18, pp. 2378-2384 (2002).
Trimbach et al., "Block Copolymer Thermoplastic Elastomers for Microcontact Printing," Langmuir, 2003, vol. 19, p. 10957.
Truskett, V. M., et. al., "Trends in Imprint Lithography for Biological Applications," TRENDS in Biotechnology, vol. 24, No. 7, Jul. 2006, pp. 312-315.
Van Poll, M. L., et al., "a Self-Assembly Approach to Chemical Micropatterning of Poly(dimethylsiloxane)," Angew. Chem. Int. Ed. 2007, 46, pp. 6634-6637.
Wang, C., et al., "One Step Fabrication and characterization of Platinum Nanopore Electrode Ensembles formed via Amphiphilic Block Copolymer Self-assembly," Electrochimica Acta 52 (2006), pp. 704-709.
Wathier, M., et al., "Dendritic Macromers as in Situ Polymerizing Biomaterials for Securing Cataract Incisions," J. Am. Chem. Soc., 2004, 126 (40), pp. 12744-12745, Abstract only.

(56) **References Cited**

OTHER PUBLICATIONS

Winesett, D.A., et al., "Tuning Substrate Surface Energies for Blends of Polystyrene and Poly(methyl methacrylate)," Langmuir 2003, 19, American Chemical Society, pp. 8526-8535.
Wipf, "Handbook of Reagents for Organic Synthesis", 2005, John Wiley & Sons Ltd., p. 320.
Wu, C.Y., et al., "Self-Assembled Two-Dimensional Block Copolymers on Pre-patterned Templates with Laser Interference Lithography," IEEE, 2007, pp. 153-154.
Xia et al., An Approach to Lithographically Defined Self-Assembled Nanoparticle Films, Advanced Materials, vol. 18, pp. 930-933 (2006).
Xia, Younan, et al., "Soft Lithography," Annu. Rev. Mater. Sci., vol. 28, pp. 153-184, 1998.
Xiao, Shuaigang., et al., "Graphoepitaxy of Cylinder-forming Block Copolymers for Use as Templates to Pattern Magnetic Metal Dot Arrays," Nanotechnology 16, IPO Publishing Ltd, UK (2005), pp. S324-S329.
Xu et al., Electric Field Alignment of Symmetric Diblock Copolymer Thin Films, Department of Polymer Science and Engineering, University of Massachusetts, 5 pages (2003).
Xu et al., Interfacial Interaction Dependence of Microdomain Orientation in Diblock Copolymer Thin Films, Macromolecules, vol. 38, pp. 2802-2805 (2005).
Xu, F.J., et al., "Surface-Initiated Atom Transfer Radical Polymerization from Halogen-Terminated Si(111) (Si-X, X=Cl, Br) Surfaces for the Preparation of Well-Defined Polymer-Si Hybrids," Langmuir, vol. 21, No. 8, pp. 3221-3225, 2005.
Xu, Ting, et al., "The Influence of Molecular Weight on Nanoporous Polymer Films," Polymer 42, Elsevier Science Ltd., (2001) pp. 9091-9095.
Yamaguchi, T., et al., "Resist-Pattern Guided Self-Assembly of Symmetric Diblock Copolymer," Journal of Photopolymer Science and Technology, vol. 19, No. 3, pp. 385-388 (2006).
Yamaguchi, Toru, et al., "Two-dimensional Arrangement of Vertically Oriented Cylindrical Domains of Diblock Copolymers Using Graphoepitaxy with Artificial Guiding Pattern Layout," Microprocesses and Nanotechnology, 2007, Conference date Nov. 5-8, 2007, pp. 434-435.
Yan, Xiaohu, et al., "Preparation and Phase Segregation of Block Copolymer Nanotube Multiblocks," J. Am. Chem. Soc., vol. 126, No. 32, 2004, American Chemical Society, pp. 10059-10066.
Yang et al., Covalently Attached Graft Polymer Monolayer on Organic Polymeric Substrate via Confined Surface Inhibition Reaction, Journal of Polymer Science—A—Polymer Chemistry Edition, Sep. 28, 2006, pp. 745-755, vol. 45, Issue 5.
Yang, Xiao M., et al., "Guided Self-Assembly of Symmetric Diblock Copolymer Films on Chemically Nanopatterned Substrates," Macromolecules 2000, vol. 33, No. 26, 2000, American Chemical Society, pp. 9575-9582.
Yang, Xiaomin, et al., "Nanoscopic Templates Using Self-assembled Cylindrical Diblock Copolymers for Patterned Media," J. Vac. Sci. Technol. B 22(6), Nov./Dec. 2004, American Vacuum Society, pp. 3331-3334.
Yu et al., Contact Printing Beyond Surface Roughness: Liquid Supramolecular Nanostamping, Advanced Materials, vol. 19, 2007, pp. 4338-4342.
Yurt, Serkan, et al., "Scission of Diblock Copolymers into Their Constituent Blocks," Macromolecules 2006, vol. 39, No. 5, 2006, American Chemical Society, pp. 1670-1672.
Zaumseil et al., "Three-Dimensional and Multilayer Nanostructures Formed by Nanotransfer Printing," Nano Letters, 2003, vol. 3, No. 9, pp. 1223-1227.
Zehner, R. W., et al., "Selective Decoration of a Phase-Separated Diblock Copolymer with Thiol-Passivated Gold Nanocrystals," Langmuir, vol. 14, No. 2, pp. 241-244, Jan. 20, 1998.
Zhang et al., "Self-Assembled Monolayers of Terminal Alkynes on Gold," J. Am. Chem. Soc., vol. 129, No. 16, pp. 4876-4877, 2007.
Zhang, Mingfu, et al., "Highly Ordered Nanoporous Thin Films from Cleavable Polystyrene-block-poly(ethylene oxide)," Adv. Mater. 2007, 19, pp. 1571-1576.
Zhang, Yuan, et al., "Phase Change Nanodot Arrays Fabricated Using a Self-Assembly Diblock Copolymer Approach," Applied Physics Letter, 91, 013104, 2007, American Institute of Physics, pp. 013104 to 013104-3.
Zhao et al., Colloidal Subwavelength Nanostructures for Antireflection Optical Coatings, Optics Letters, vol. 30, No. 14, pp. 1885-1887 (2005).
Li, H, W. Huck; "Ordered Block-Copolymer Assembly Using Nanoimprint Lithography". Nano. Lett. (2004), vol. 4, No. 9, p. 1633-1636.
Cheng, J., C. Ross, H. Smith, E. Thomas; "Templated Self-Assembly of Block Copolymers: Top-Down Helps BottomUp". Adv. Mater. (2006), 18, p. 2505-2521.

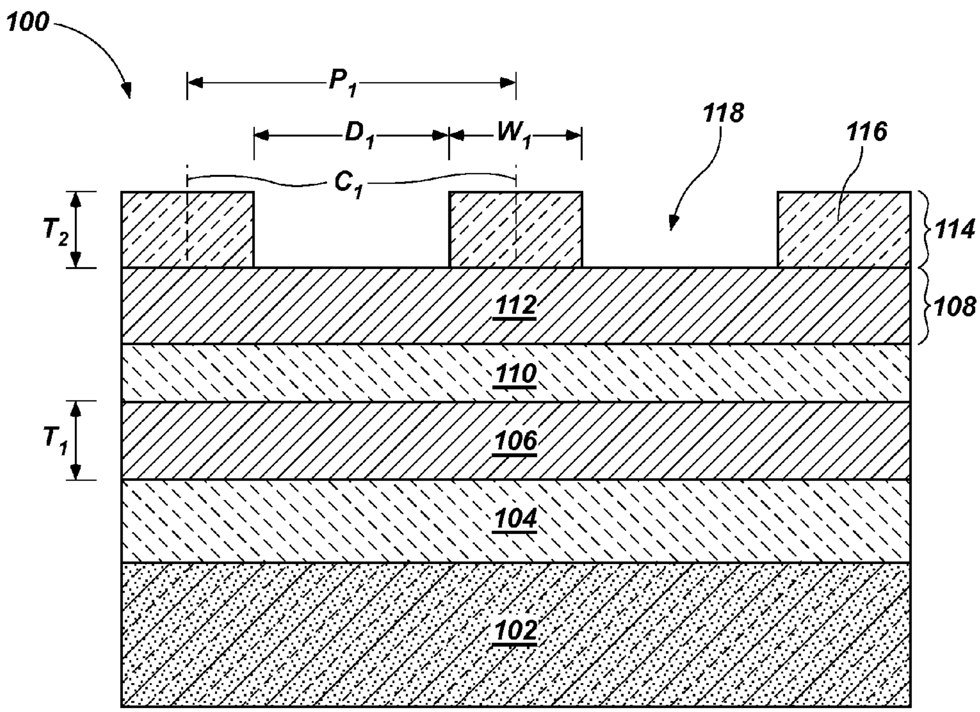

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FIG. 1

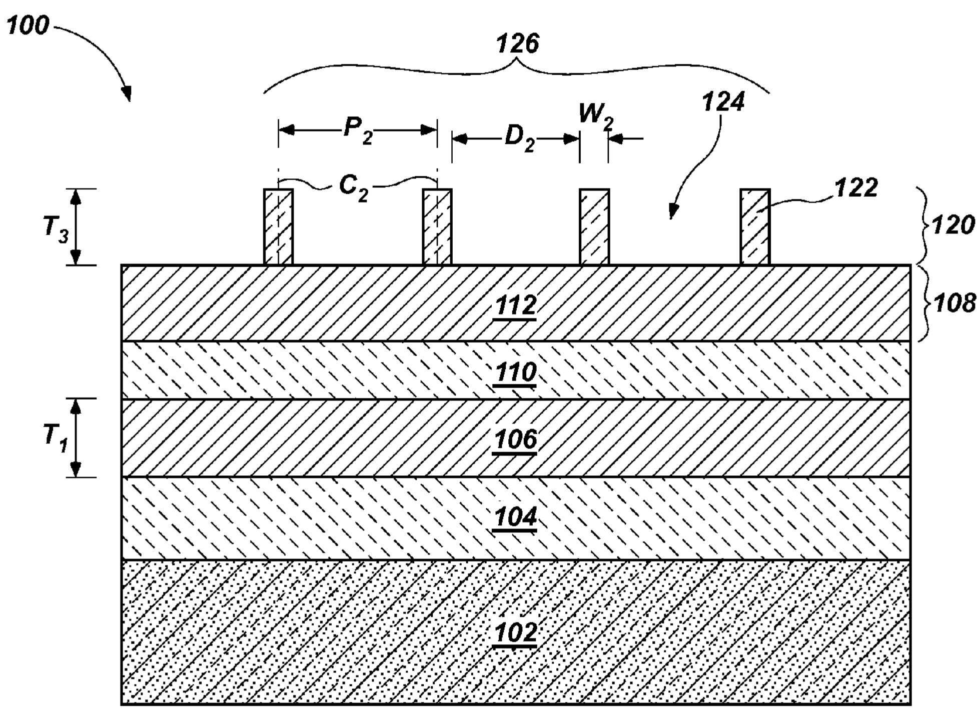
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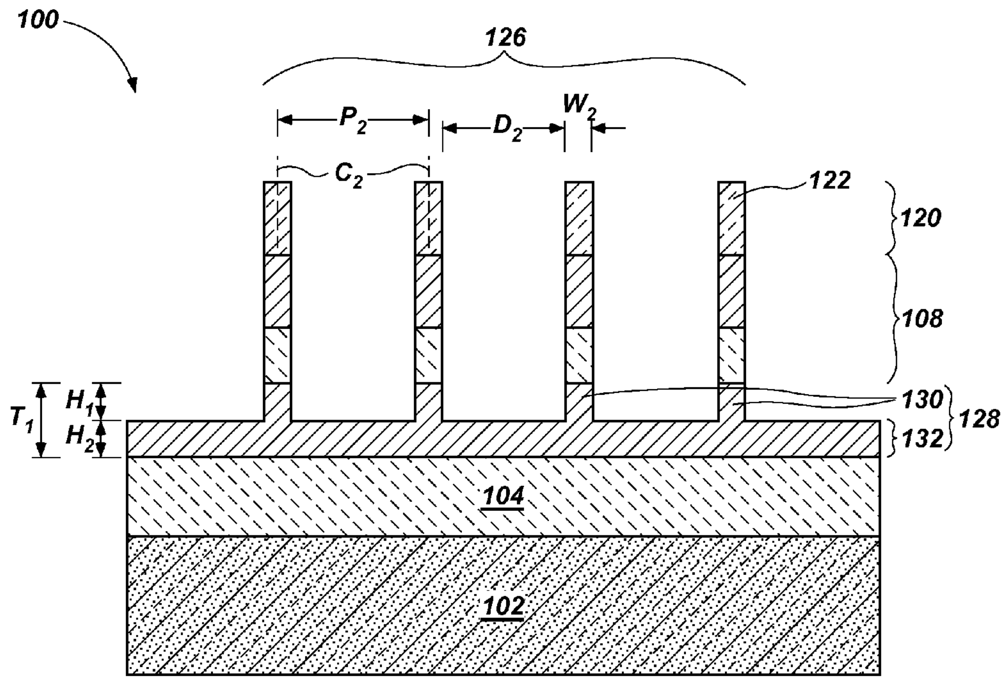
FIG. 2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T1
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H2
104
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FIG. 3

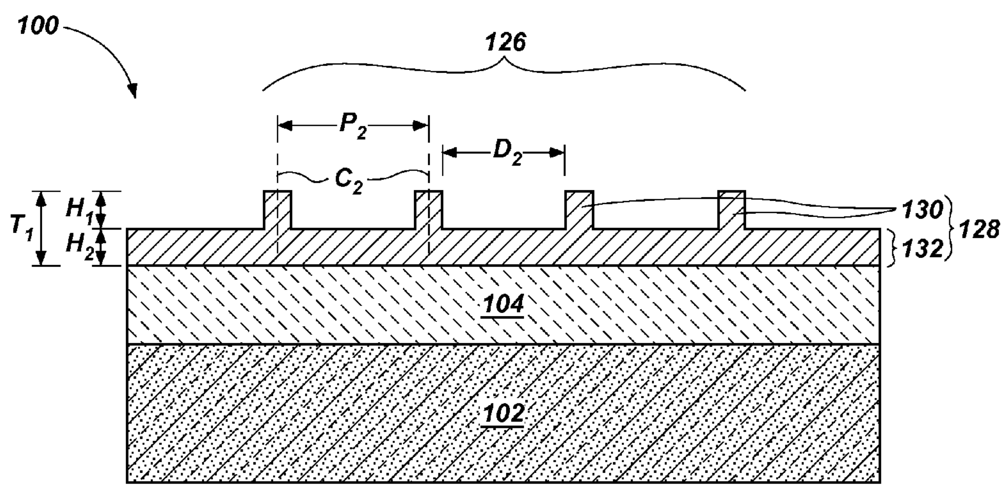
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FIG. 4

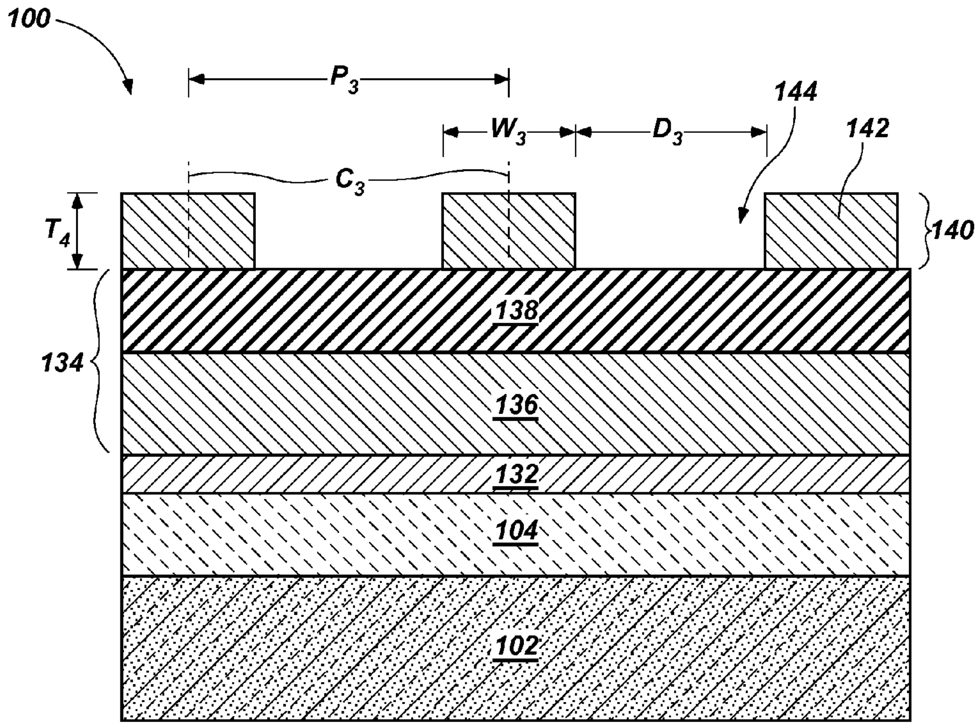
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FIG. 5

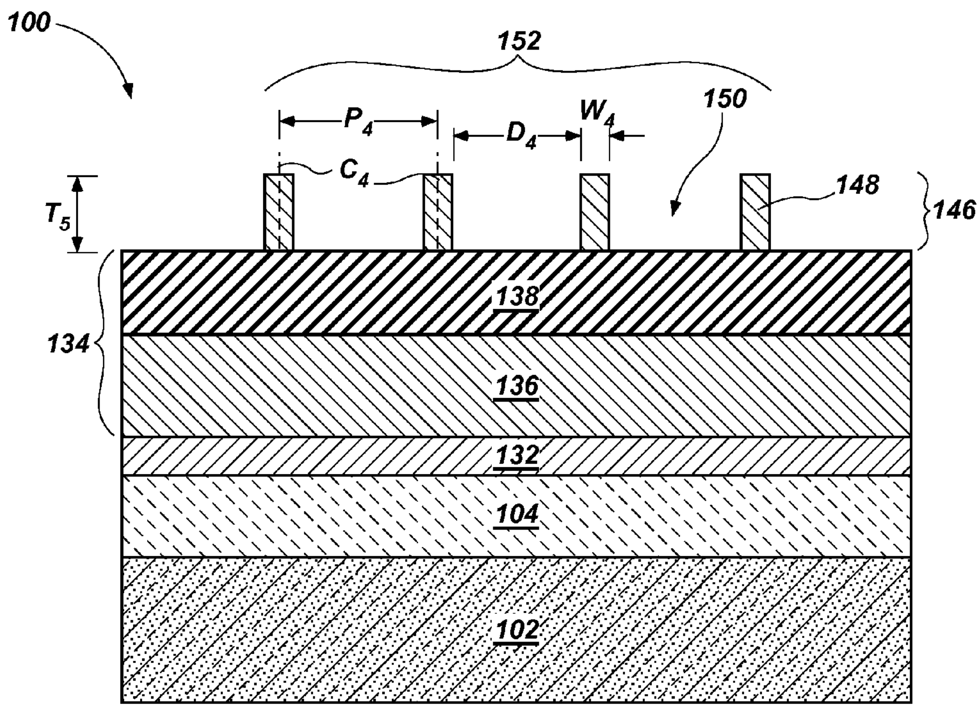
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FIG. 6

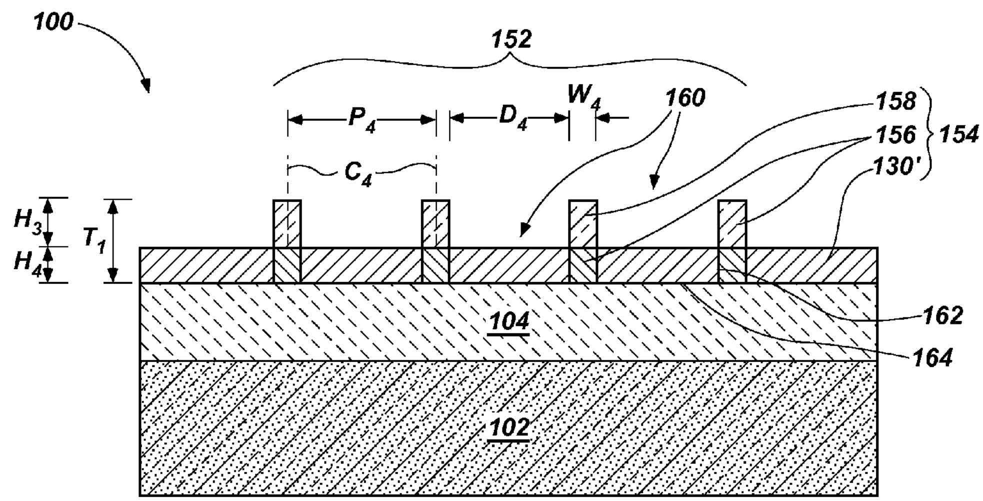
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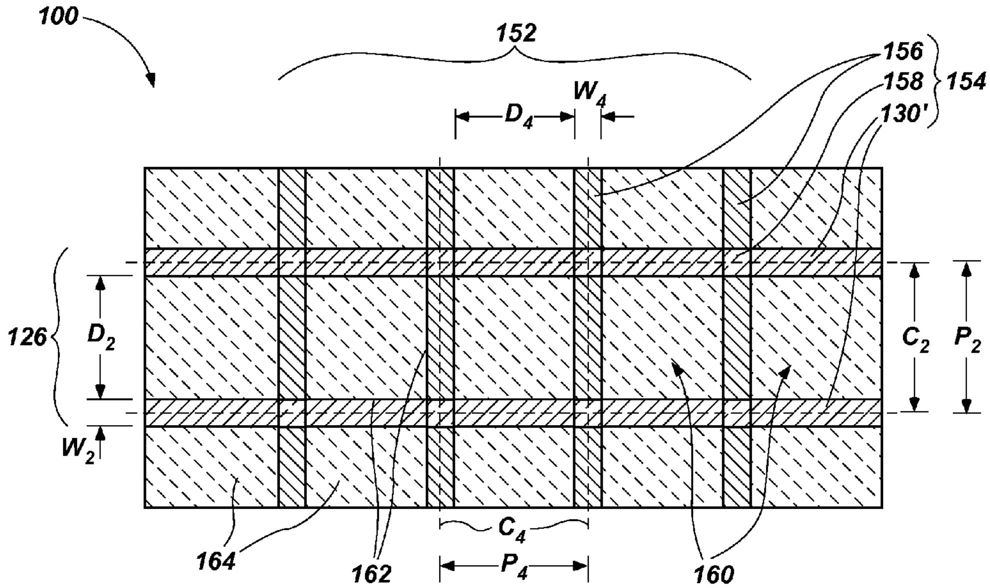
FIG. 7A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P4
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FIG. 7B

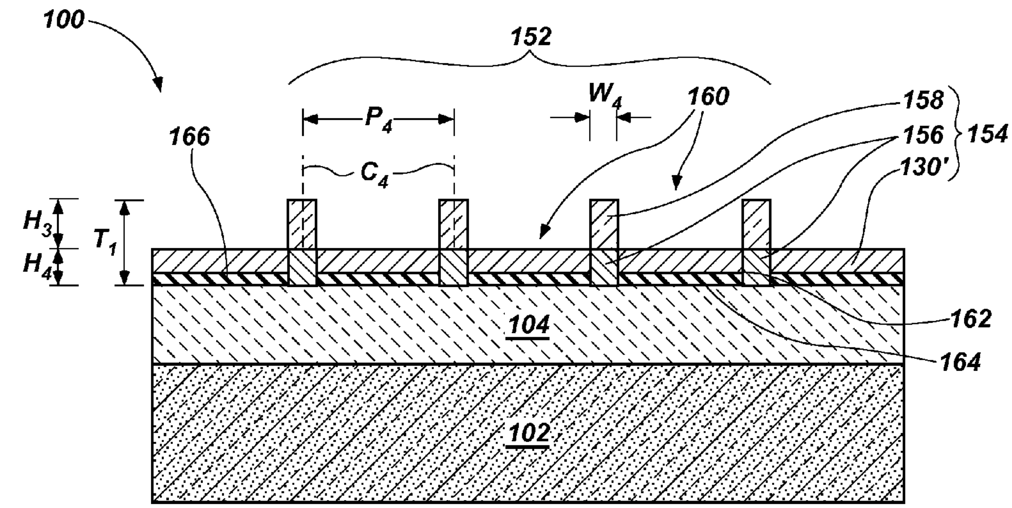
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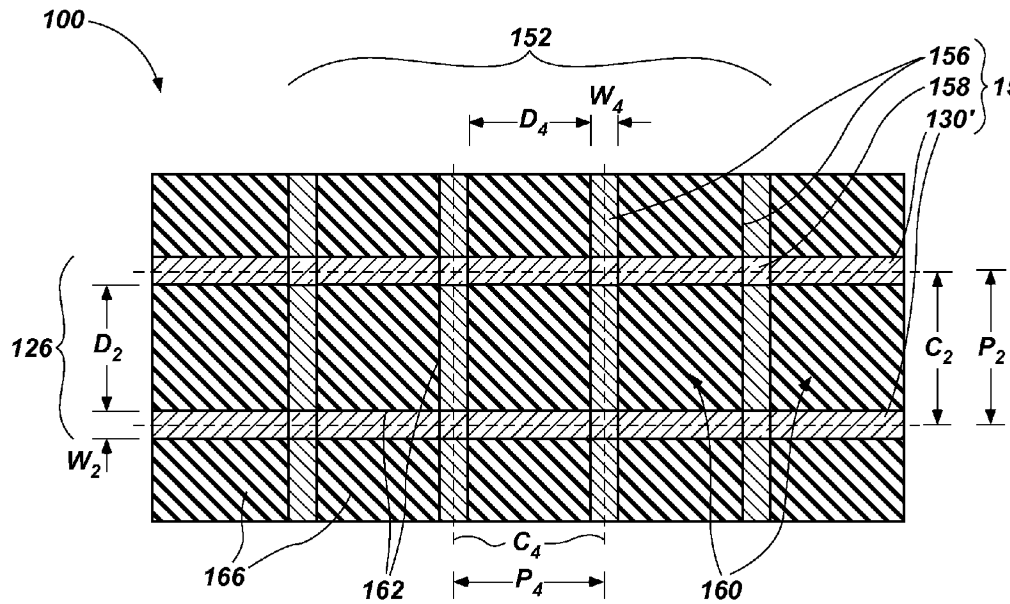
FIG. 8A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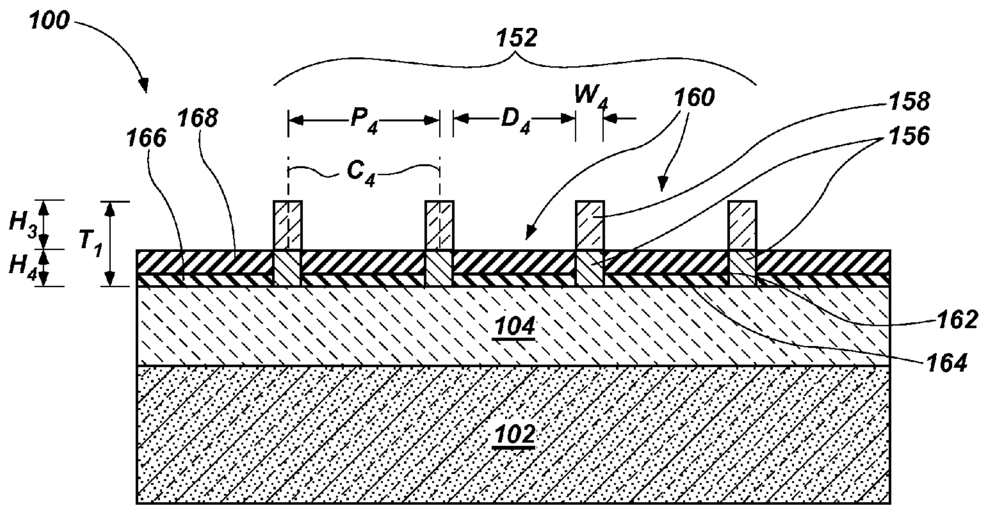
162
160

FIG. 8B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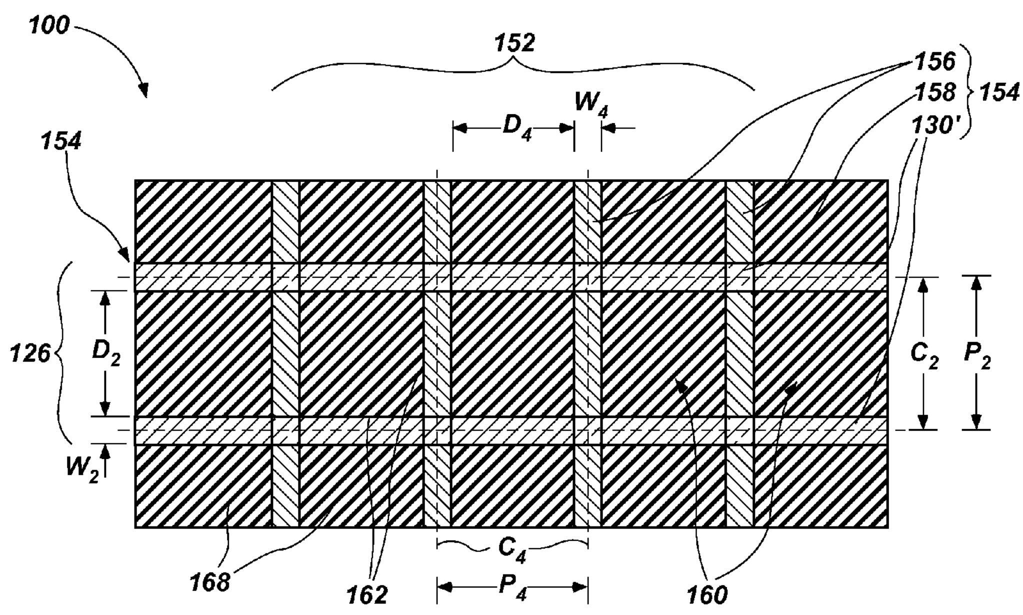
164

FIG. 9A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C_4
P_4
160

FIG. 9B

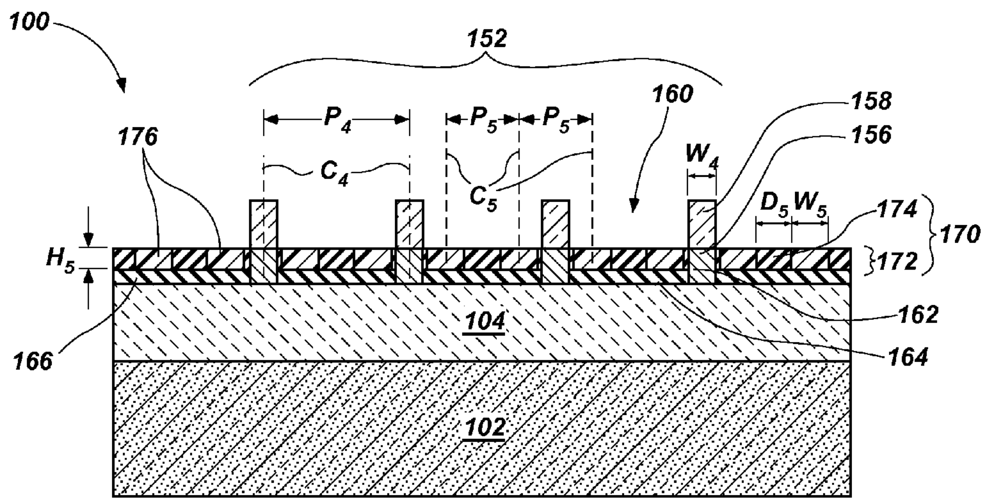

FIG. 10A

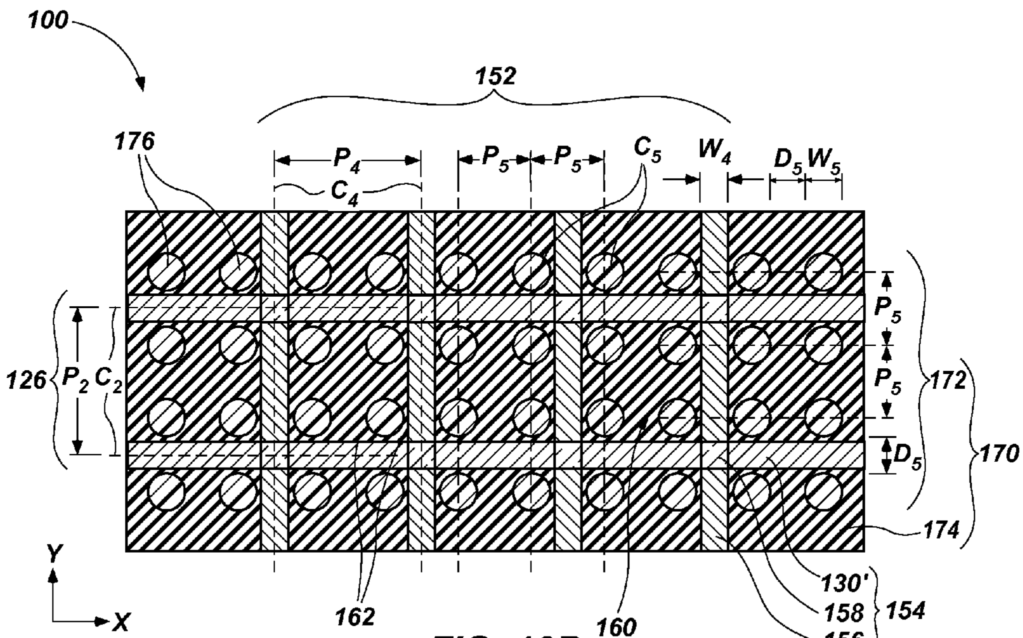

FIG. 10B

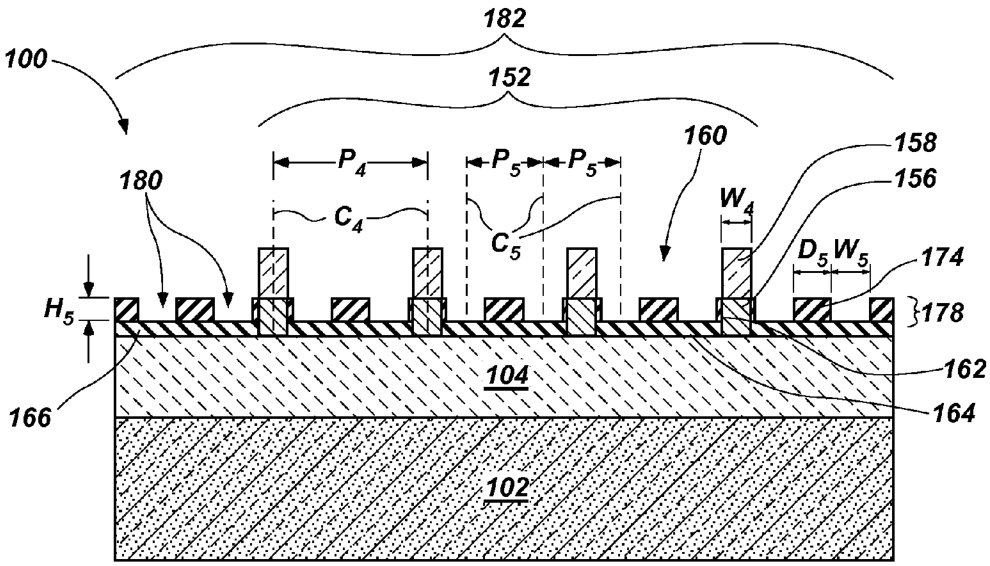

FIG. 11A

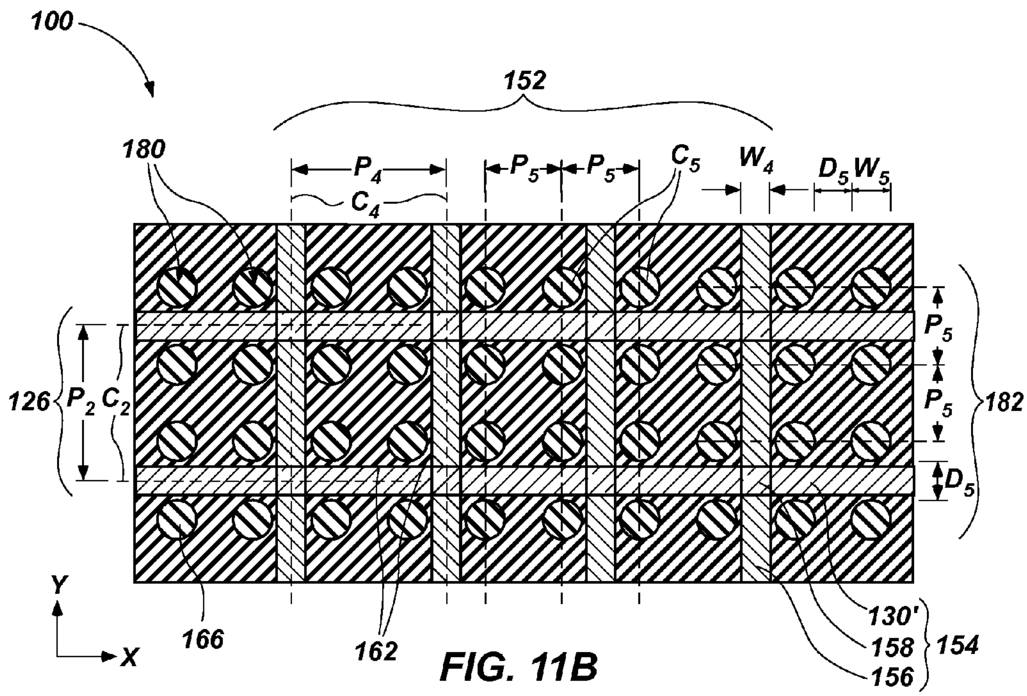

FIG. 11B

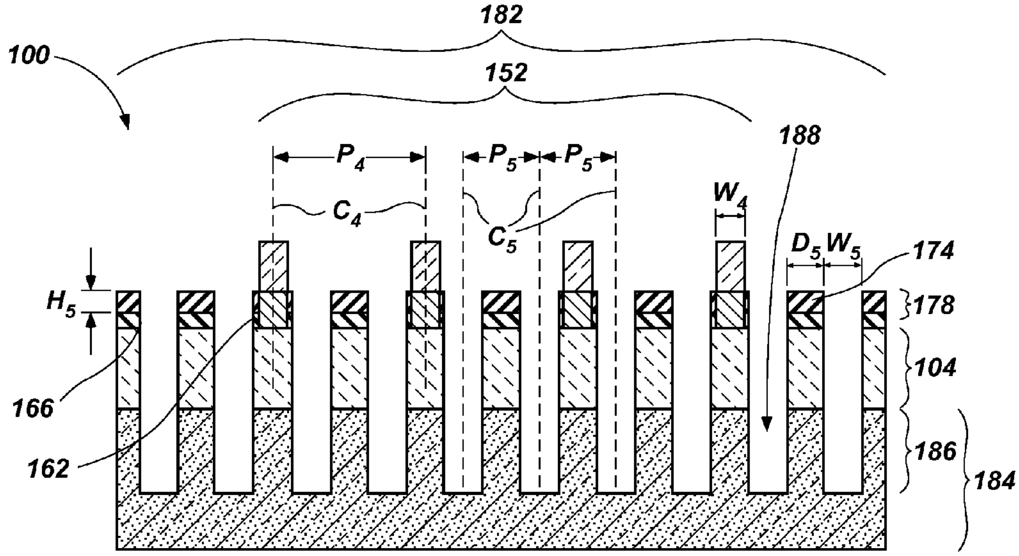

FIG. 12A

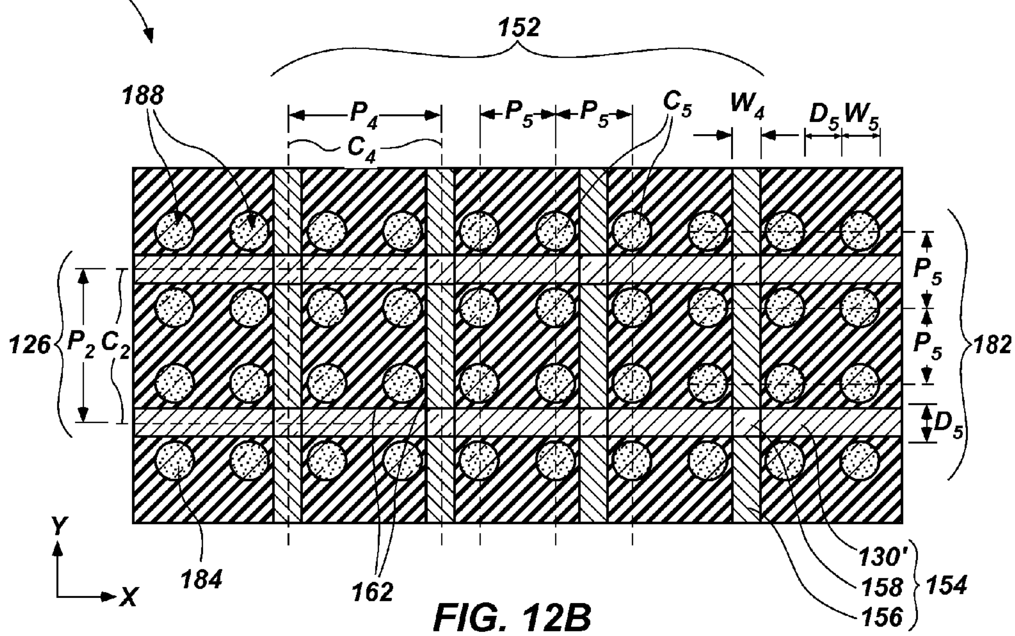

FIG. 12B

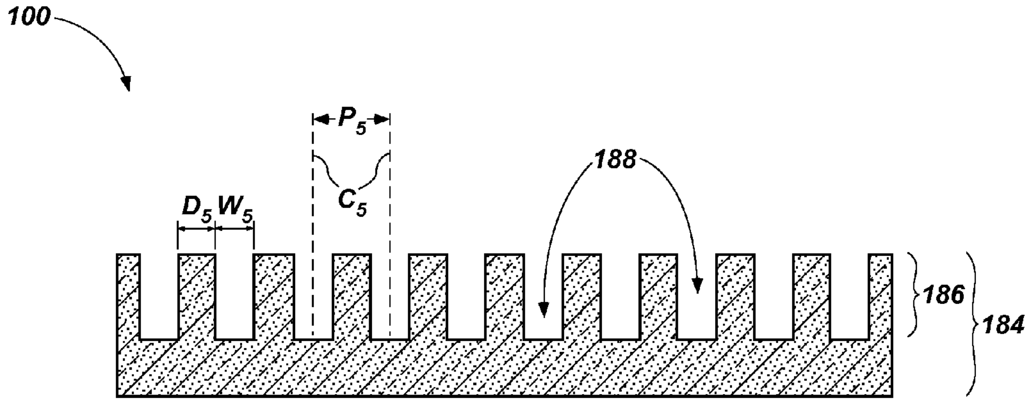

FIG. 13A

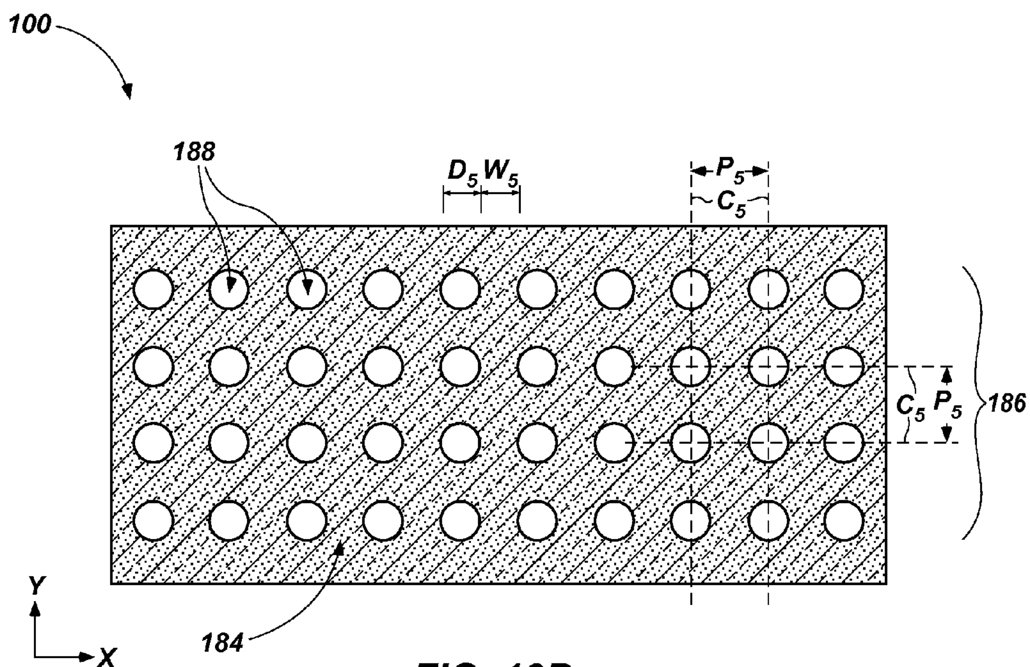

FIG. 13B

METHODS OF FORMING AN ARRAY OF OPENINGS IN A SUBSTRATE, AND RELATED METHODS OF FORMING A SEMICONDUCTOR DEVICE STRUCTURE

TECHNICAL FIELD

Embodiments of the disclosure relate to the field of semiconductor device design and fabrication. More specifically, embodiments of the disclosure relate to methods of forming an array of openings in a substrate, to related methods of forming a semiconductor device structure, and to a related semiconductor device structure.

BACKGROUND

A continuing goal of integrated circuit fabrication is to decrease the dimensions thereof. Integrated circuit dimensions can be decreased by reducing the dimensions and spacing of the constituent features or structures thereof. For example, by decreasing the dimensions and spacing of features (e.g., storage capacitors, access transistors, access lines, etc.) of a memory device, the overall dimensions of the memory device may be decreased while maintaining or increasing the storage capacity of the memory device.

Reducing the dimensions and spacing of semiconductor device features places ever increasing demands on the methods used to form the features. For example, due to limitations imposed by optics and radiation wavelengths, many conventional photolithographic methods cannot facilitate the formation of features having critical dimensions (e.g., widths, diameters, etc.) of less than about sixty (60) nanometers (nm). Electron beam (E-beam) lithography and extreme ultraviolet (EUV) lithography have been used to form features having critical dimensions less than 60 nm, but generally require complex processes and significant costs.

One approach for achieving features having critical dimensions of less than about 60 nm has been the use of pitch density multiplication processes, such as pitch density doubling processes. In a conventional pitch density doubling process, a photolithographic process is used to form photoresist lines over a sacrificial material over a substrate. The sacrificial material is etched using the photoresist lines to form mandrels, the photoresist lines are removed, spacers are formed on sides of the mandrels, and the mandrels are removed. The remaining spacers are used as a mask to pattern the substrate. Where the initial photolithography process formed one feature and one trench across a particular width of the substrate, after pitch density doubling, the same width of the substrate can include two smaller features and two smaller trenches, the width of each of the smaller trenches defined by the width of the spacers. Thus, the use of pitch density doubling can halve the minimum critical dimensions of features formed by the photolithographic processes, resulting in features having minimum critical dimension of about 30 nm. However, to achieve features having critical dimensions less than about 30 nm, the pitch density doubling process needs to be repeated (i.e., the process becomes a pitch density quadrupling process), significantly increasing processing time as well as energy and material costs.

Another approach for achieving semiconductor device features having critical dimensions of less than about 60 nm has been the use of self-assembling (SA) block copolymers. For example, an SA block copolymer deposited within a trench having particular graphoepitaxial characteristics (e.g., dimensions, wetting properties, etc.) may be annealed to form select morphology (e.g., spherical, lamellar, cylindrical, etc.) domains of one polymer block of the SA block copolymer within a matrix domain of another polymer block of the SA block copolymer. The select morphology domains or the matrix domain can be selectively removed, and the remaining select morphology domains or matrix domain utilized as an etch mask for patterning features into an underlying substrate. As the dimensions of the select morphology domains and the matrix domain are at least partially determined by the chain length of the SA block copolymer, feature dimensions much smaller than 60 nm are achievable (e.g., dimensions similar to those achievable through E-beam and EUV lithography processes). Such methods have, for example, been used to form close-packed, hexagonal arrays of openings in an underlying substrate. However, certain semiconductor device structures may utilize different (i.e., non-hexagonal) array configurations. For example, Dynamic Random Access Memory (DRAM) device structures may utilize rectilinear arrays of openings (e.g., contact openings) rather than hexagonal arrays of openings.

A need, therefore, exists for new, simple, and cost-efficient methods of forming a rectilinear array of openings for a semiconductor device structure, such as, for example, a rectilinear contact array for a memory device structure, that enables the formation of the closely packed openings having critical dimensions (e.g., widths, diameters, etc.) less than or equal to about 30 nm.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

FIGS. **1** through **13**B are cross-sectional (i.e., FIGS. **1** through **7**A, **8**A, **9**A, **10**A, **11**A, **12**A, and **13**A) and top-down (FIGS. **7**B, **8**B, **9**B, **10**B, **11**B, **12**B, and **13**B) views of a semiconductor device structure in accordance with embodiments of the disclosure, and illustrate a method of forming a rectilinear array of openings in a substrate of a semiconductor device structure, in accordance with embodiments of the disclosure.

DETAILED DESCRIPTION

Methods of forming a rectilinear array of openings (e.g., a rectilinear contact array) in a substrate are disclosed, as are related methods of forming a semiconductor device structure including the rectilinear array of openings, and a related semiconductor device structure including the rectilinear array of openings. In some embodiments, a template structure having the dimensions, spacing, and wetting characteristics for forming a rectilinear array of cylindrical domains of a first polymer within a matrix domain of a second polymer from a block copolymer material may be formed over a substrate by way of pitch density doubling processes. An appropriate block copolymer material may be deposited in wells defined by the template structure, the block polymer material may be processed (e.g., annealed) to form a self-assembled block copolymer material, and the cylindrical domains of the first polymer may be selectively removed to form a patterned polymer material. The patterned polymer material may be used as a mask to form a rectilinear array of openings in the substrate. The openings of the rectilinear array may each have substantially the same width, such as less than or equal to about 30 nm, and a pitch between adjacent openings may be substantially uniform, such as less than or equal to about 50 nm. The rectilinear array of openings may, for example, be utilized in a dynamic random access memory (DRAM) device. The methods of forming the rectilinear array of openings disclosed herein may decrease processing complexity, steps, and cost relative to conventional methods of forming a rectilinear array of openings. The methods of the disclosure may enable increased opening density, facilitating increased performance in semiconductor device structures (e.g., DRAM cells) and semiconductor devices (e.g., DRAM devices) that rely on high opening (e.g., contact) density.

As used herein, the term "rectilinear array" means and includes an array including rows of features that intersect columns of features at about a ninety degree (90°) angle. Accordingly, a "rectilinear array of openings" means and includes an array of openings including rows of openings that intersect columns of openings at about a ninety degree (90°) angle.

As used herein, the term "pitch" refers to the distance between identical points in two adjacent (i.e., neighboring) features. By way of non-limiting example, the pitch between two adjacent cylindrical domains may be viewed as the sum of the radii of the adjacent cylindrical domains and any space between the adjacent cylindrical domains. Stated another way, the pitch in the foregoing example may be characterized as the distance between the centers of the adjacent cylindrical domains.

As used herein, relational terms, such as "first," "second," "over," "top," "bottom," "underlying," etc., are used for clarity and convenience in understanding the disclosure and accompanying drawings and does not connote or depend on any specific preference, orientation, or order, except where the context clearly indicates otherwise.

As used herein, the term "substantially," in reference to a given parameter, property, or condition, means to a degree that one of ordinary skill in the art would understand that the given parameter, property, or condition is met with a small degree of variance, such as within acceptable manufacturing tolerances.

The following description provides specific details, such as material types, material thicknesses, and processing conditions in order to provide a thorough description of embodiments of the disclosure. However, a person of ordinary skill in the art will understand that the embodiments of the present disclosure may be practiced without employing these specific details. Indeed, the embodiments of the present disclosure may be practiced in conjunction with conventional fabrication techniques employed in the industry. In addition, the description provided below does not form a complete process flow for manufacturing a semiconductor device. The semiconductor device structures described below do not form a complete semiconductor device. Only those process acts and structures necessary to understand the embodiments of the disclosure are described in detail below. Additional acts to form the complete semiconductor device from the semiconductor device structures may be performed by conventional fabrication techniques. Also note, any drawings accompanying the present application are for illustrative purposes only, and are thus not drawn to scale. Additionally, elements common between figures may retain the same numerical designation.

FIGS. **1** through **13**B, are simplified cross-sectional (i.e., FIGS. **1** through **7**A, **8**A, **9**A, **10**A, **11**A, **12**A, and **13**A) and top-down (i.e., FIGS. **7**B, **8**B, **9**B, **10**B, **11**B, **12**B, and **13**B) views illustrating embodiments of a method of forming a rectilinear array of openings in a substrate of a semiconductor device structure, such as a rectilinear contact array for a DRAM device structure. With the description provided below, it will be readily apparent to one of ordinary skill in the art that the methods described herein may be used in various devices. In other words, the methods of the disclosure may be used whenever it is desired to form a rectilinear array of openings in a substrate.

Referring to FIG. **1**, a semiconductor device structure **100** may include a substrate **102**, a substrate masking material **104** over the substrate **102**, a template material **106** over the substrate masking material **104**, template masking materials **108** over the template material **106**, and a patterned photoresist material **114** over the template masking materials **108**. As used herein, the term "substrate" means and includes a base material or other construction upon which additional materials are formed. The substrate **102** may be a semiconductor substrate, a base semiconductor layer on a supporting structure, a metal electrode or a semiconductor substrate having one or more layers, structures or regions formed thereon. The substrate **102** may be a conventional silicon substrate or other bulk substrate comprising a layer of semiconductive material. As used herein, the term "bulk substrate" means and includes not only silicon wafers, but also silicon-on-insulator (SOI) substrates, such as silicon-on-sapphire (SOS) substrates and silicon-on-glass (SOG) substrates, epitaxial layers of silicon on a base semiconductor foundation, and other semiconductor or optoelectronic materials, such as silicon-germanium, germanium, gallium arsenide, gallium nitride, and indium phosphide. The substrate **102** may be doped or undoped.

The substrate masking material **104** may be a material that is selectively etchable relative to a domain of a self-assembled block copolymer material to be formed over the substrate masking material **104**, as described in further detail below. As used herein, a material is "selectively etchable" relative to another material if the material exhibits an etch rate that is at least about five times (5×) greater than the etch rate of another material, such as about ten times (10×) greater, about twenty times (20×) greater, or about forty times (40×) greater. The substrate **102** may be selectively etchable relative to the substrate masking material **104**. In some embodiments, the substrate masking material **104** is formed of and includes amorphous carbon. A thickness of the substrate masking material **104** may be selected at least partially based on the etch chemistries and process conditions used to form the rectilinear array of openings of the disclosure, as described in further detail below. By way of non-limiting example, the substrate masking material **104** may have a thickness within a range of from about 100 nanometers (nm) to about 1000 nm, such as from about 200 nm to about 800 nm, or from about 300 nm to about 700 nm. In some embodiments, the substrate masking material **104** has a thickness of about 600 nm.

The template material **106** may be a material that, upon being patterned, facilitates forming a self-assembled block copolymer material including a rectilinear array of cylindrical domains of a first polymer within a matrix domain of a second polymer, as described in further detail below. The template material **106** may, for example, be a material that is preferential wetting to a polymer block (e.g., a minority block, or a majority block) of the block copolymer material (as well as any homopolymers included in the block copolymer material that are of the same polymer type as the polymer block). As a non-limiting example, template material **106** may be formed of and include at least one of a silicon oxide, a silicon nitride, a silicon oxycarbide, and a dielectric anti-reflective coating (DARC) (e.g., a silicon oxynitride, such as a silicon-rich silicon oxynitride). In some embodiments, the template material **106** is selected to be preferential wetting toward a polymethylmethacrylate (PMMA) block of poly (styrene-b-methylmethacrylate) (PS-b-PMMA). In additional embodiments, the template material **106** is selected to be preferential wetting toward a polydimethylsiloxane

(PDMS) block of poly(styrene-block-dimethylsiloxane) (PS-b-PDMS). The template material **106** may have a thickness T_1 conducive to the patterning of the template material **106** to form a template structure, as described in further detail below. By way of non-limiting example, the thickness T_1 of the template material **106** may be within a range of from about 50 nanometers (nm) to about 500 nm, such as from about 50 nm to about 100 nm. In some embodiments, the thickness T_1 of the template material **106** is about 75 nm.

The template masking materials **108** may include materials that aid in the patterning of the template material **106**. For example, as depicted in FIG. **1**, the template masking materials **108** may include a protective material **110** over the template material **106** and a hard mask material **112** over the protective material **110**. Each of the protective material **110** and the hard mask material **112** may be selectively etchable relative to spacers to be formed over the template masking materials **108**. The protective material **110** and the hard mask material **112** may be the same as or different than the substrate masking material **104** and the template material **106**, respectively. By way of non-limiting example, the protective material **110** may be formed of and include amorphous carbon, and the hard mask material **112** may be formed of and include at least one of silicon, a silicon oxide, a silicon nitride, a silicon oxycarbide, aluminum oxide, and a silicon oxynitride. The protective material **110** may have a thickness within a range of from about 50 nm to about 300 nm, such as from about 60 nm to about 200 nm. The hard mask material **112** may have a thickness within a range of from about 10 nm to about 50 nm, such as from about 10 nm to about 40 nm. In some embodiments, the protective material **110** has a thickness of about 70 nm, and the hard mask material **112** has a thickness of about 26 nm. In embodiments where the template material **106** is selectively etchable relative to a spacer material to be formed thereover, at least a portion of the template masking materials **108** (e.g., at least one of the protective material **110** and the hard mask material **112**) may, optionally, be omitted.

Each of the substrate **102**, the substrate masking material **104**, the template material **106**, and the template masking materials **108** (if present) may be formed using conventional processes including, but not limited to, physical vapor deposition ("PVD"), chemical vapor deposition ("CVD"), atomic layer deposition ("ALD"), or spin-coating. PVD includes, but is not limited to, sputtering, evaporation, or ionized PVD. Such processes are known in the art and, therefore, are not described in detail herein.

The patterned photoresist material **114** may include parallel photoresist lines **116** separated by first trenches **118**. As used herein, the term "parallel" means substantially parallel. Each of the parallel photoresist lines **116** may be formed of and include a conventional photoresist, such as a photoresist compatible with 13.7 nm, 157 nm, 193 nm, 248 nm, or 365 nm wavelength systems, a photoresist compatible with 193 nm wavelength immersion systems, or a photoresist compatible with electron beam lithographic systems. By way of non-limiting example, each of the parallel photoresist lines **116** may be formed of and include an argon fluoride (ArF) sensitive photoresist (i.e., a photoresist suitable for use with an ArF light source), or a krypton fluoride (KrF) sensitive photoresist (i.e., a photoresist suitable for use with a KrF light source).

Each of the parallel photoresist lines **116** may have substantially the same width W_1, thickness T_2, and length (not shown). In addition, the parallel photoresist lines **116** may be regularly spaced by a distance D_1 (i.e., the width of each of the first trenches **118**). Accordingly, a pitch P_1 between centerlines C_1 of adjacent parallel photoresist lines may be substantially uniform throughout the patterned photoresist material **114**. The dimensions and spacing of the parallel photoresist lines **116** may be selected to provide desired dimensions and spacing to parallel spacers to be formed on the parallel photoresist lines **116**. For example, the width W_1 and the centerline C_1 location of each of the parallel photoresist lines **116** may be selected to facilitate the formation of parallel spacers exhibiting smaller dimensions and decreased pitch relative to the parallel photoresist lines **116**, as described in further detail below. In some embodiments, the width W_1 of each of the parallel photoresist lines **116** is about 50 nm, the distance D_1 between adjacent parallel photoresist lines is about 70 nm, and the pitch P_1 between adjacent parallel photoresist lines is about 120 nm.

The patterned photoresist material **114** may be formed using conventional processing techniques, which are not described in detail herein. By way of non-limiting example, a photoresist material (not shown) may be formed over the template masking materials **108** and exposed to an appropriate wavelength of radiation through a reticle (not shown) and then developed. The parallel photoresist lines **116** may correlate to portions of the photoresist material remaining after the development, and the first trenches **118** may correlate to portions of the photoresist material removed during the development.

Referring to next to FIG. **2**, the patterned photoresist material **114** (FIG. **1**) may be used to form a patterned spacer material **120** including parallel spacers **122** separated by second trenches **124**. The patterned spacer material **120** may define a first pattern **126** to be transferred to the template material **106**, as described in further detail below. Each of the parallel spacers **122** may be formed of and include a material suitable for use as a mask for selectively removing (e.g., etching) of portions of the template masking materials **108** and the template material **106**. By way of non-limiting example, each of the parallel spacers **122** may be formed of and include a silicon oxide or a silicon nitride. In some embodiments, each of the parallel spacers **122** is formed of and includes a silicon oxide.

Each of the parallel spacers **122** may have substantially the same width W_2, thickness T_3, and length (not shown). The thickness T_3 of each of the parallel spacers **122** may be substantially the same as the thickness T_2 of each of the parallel photoresist lines **116** (FIG. **1**). In addition, the parallel spacers **122** may be oriented parallel to one another, and may be regularly spaced by a distance D_2 (i.e., the width of each of the second trenches **124**) that is substantially the same as the width W_1 of each of the parallel photoresist lines **116**. A pitch P_2 between centerlines C_2 of adjacent parallel spacers may be equal to about half of the pitch P_1 between the centerlines C_1 of adjacent photoresist lines of the patterned photoresist material **114** (FIG. **1**). The dimensions and spacing of the parallel spacers **122** may be selected to provide desired dimensions and spacing for features of a template structure to be formed using the patterned spacer material **120**, as described in further detail below. The width W_2 of each of the parallel spacers **122** may be within a range of from about 20 percent to about 40 percent of a target (e.g., desired) pitch between adjacent openings of a rectilinear array of openings to be formed using the template structure, such as from about 20 percent to about 30 percent of the target pitch. The distance D_2 between each of the parallel spacers **122** may be within a range of from about 180 percent to about 160 percent of the target pitch between adjacent openings of the rectilinear array of openings to be formed, such as from about 180 percent to about 170 percent of the target pitch. The pitch P_2 between adjacent parallel spacers of the patterned spacer material **120** may be about two times (2×) the target pitch between adjacent openings of the rectilinear array of openings to be formed.

By way of non-limiting example, if a target pitch between adjacent openings of the rectilinear array of openings to be formed is about 30 nm, the width W_2 of each of the parallel spacers **122** may be within a range of from about 6 nm to about 12 nm, the distance D_2 between adjacent parallel spacers of the patterned spacer material **120** may be within a range of from about 54 nm and about 48 nm, and the pitch P_2 between centerlines C_2 of adjacent parallel spacers of the patterned spacer material **120** may be about 60 nm. In some embodiments, the width W_2 of each of the parallel spacers **122** is about 10 nm, the distance D_2 between adjacent parallel spacers of the patterned spacer material **120** is about 50 nm, and the pitch P_2 between adjacent parallel spacers of the patterned spacer material **120** is about 60 nm.

A pitch density doubling process may be utilized to form the patterned spacer material **120** using the patterned photoresist material **114**. For example, referring collectively to FIGS. **1** and **2**, a spacer material (not shown) may be conformally formed (e.g., deposited using a PVD process, a CVD process, an ALD process, or a spin-coating process) over exposed surfaces of the parallel photoresist lines **116** and the template masking materials **108**. A thickness of the spacer material may correspond to the width W_2 of the parallel spacers **122** to be formed. An anisotropic etching process may be performed to remove the spacer material from horizontal surfaces of the parallel photoresist lines **116** and the template masking materials **108**, while maintaining the spacer material on vertical surfaces of the parallel photoresist lines **116**. As used herein, each of the terms "horizontal" and "lateral" means and includes extending in a direction substantially parallel to the substrate **102**, regardless of the orientation of the substrate **102**. Accordingly, as used herein, each of the terms "vertical" and "longitudinal" means and includes extending in a direction substantially perpendicular to the substrate **102**, regardless of the orientation of the substrate **102**. The parallel photoresist lines **116** may then be removed (e.g., etched, such as dry etched with a silicon-dioxide-containing plasma), resulting in the patterned spacer material **120**.

In additional embodiments, the patterned spacer material **120** may be formed using structures other than the parallel photoresist lines **116** of the patterned photoresist material **114**. Such structures may, for example, be utilized if forming the spacer material over exposed surfaces of the parallel photoresist lines **116** would damage or degrade (e.g., thermally degrade) the parallel photoresist lines **116**. By way of non-limiting example, a pattern defined by the patterned photoresist material **114** may be transferred (e.g., by way of at least one etching process) to the template masking materials **108** to form a patterned template masking material (not shown). The patterned spacer material **120** may then be formed using the patterned template masking material through a process substantially similar to that described above in relation to forming the patterned spacer material **120** using the patterned photoresist material **114**.

Referring to FIG. **3**, the first pattern **126** defined by the patterned spacer material **120** may be transferred or extended into the template material **106** (FIG. **2**) to form an intermediate template structure **128** including parallel features **130** protruding from a base **132**. The parallel features **130** may have substantially the same width W_2, length (not shown), and pitch P_2 as each of the parallel spacers **122**. A height H_1 of each of the parallel features **130** may be within a range of from about 55 percent to about 45 percent of the thickness T_1 of the template material **106**. A height H_2 of the base **132** may be equal to the difference between the height H_1 of each of the parallel features **130** and the thickness T_1 of the template material **106**. In some embodiments, the width W_2 of each of the parallel features **130** is about 10 nm, the pitch P_2 between adjacent parallel features is about 60 nm, the height H_1 of each of the parallel features **130** is about 35 nm, and the height H_2 of the base **132** is about 40 nm.

To form the intermediate template structure **128**, the parallel spacers **122** of the patterned spacer material **120** may be used as a mask for at least one etching process (e.g., an anisotropic etching process) to substantially remove unmasked portions (i.e., portions not underlying the parallel spacers **122**) of each of the template masking materials **108** and the template material **106**. The unmasked portions of the template masking materials **108** may be completely removed, and the unmasked portions of the template material **106** may be partially removed. The etching process may, for example, extend the first pattern **126** from about 45 percent to about 55 percent of the way through the template material **106**. As a non-limiting example, if the thickness T_1 of the template material **106** is about 75 nm, the first pattern **126** may be extended from about 35 nm to about 40 nm into the template material **106**.

Following the formation of the intermediate template structure **128**, remaining portions of the parallel spacers **122** and the template masking materials **108** may be removed, as depicted in FIG. **4**. The remaining portions of the parallel spacers **122** and the template masking materials **108** may be removed using conventional processes, such as conventional etching processes, which are not described in detail herein.

Referring to FIG. **5**, which illustrates a cross-sectional view of the semiconductor device structure **100** taken from a viewpoint approximately 90 degrees clockwise of that of FIGS. **1** through **4**, additional template masking materials **134** may be formed over the intermediate template structure **128**, and another patterned photoresist material **140** may be formed over the additional template masking materials **134**. In FIG. **5**, the base **132** of the intermediate template structure **128** is shown, but the parallel features **130** are not illustrated because they are covered by the additional template masking materials **134**. The additional template masking materials **134** may include materials that aid in further patterning the intermediate template structure **128** (FIG. **4**). For example, the additional template masking materials **134** may include an additional protective material **136** over the intermediate template structure **128**, and an additional hard mask material **138** over the additional protective material **136**. Each of the additional protective material **136** and the additional hard mask material **138** may be selectively etchable relative to additional parallel spacers to be formed over the additional template masking materials **134**. The additional protective material **136** and the additional hard mask material **138** may be the same as or different than the protective material **110** and the hard mask material **112** previously described with reference to FIG. **1**, respectively. By way of non-limiting example, the additional protective material **136** may be formed of and include amorphous carbon, and the additional hard mask material **138** may be formed of and include at least one of silicon, a silicon oxide, a silicon nitride, a silicon oxycarbide, aluminum oxide, and a silicon oxynitride.

The additional protective material **136** may have a thickness sufficient to cover and surround each of the parallel features **130** (FIG. **4**) of the intermediate template structure **128**, such as a thickness within a range of from about 40 nm to about 80 nm, or from about 50 nm to about 60 nm. The additional hard mask material **138** may have a thickness within a range of from about 10 nm to about 50 nm, such as from about 10 nm to about 40 nm. In some embodiments, the additional hard mask material **138** has a thickness of about 80 nm, and the additional hard mask material **138** has a thickness of about 26 nm. In embodiments where the intermediate template structure **128** is selectively etchable relative to an additional spacer material to be formed thereover, at least a portion of the additional template masking materials **134** (e.g., the additional hard mask material **138**) may, optionally, be omitted. The additional template masking materials **134** may be formed using conventional processes (e.g., CVD, PVD, ALD, or spin-coating), which are not described in detail herein.

The another patterned photoresist material **140** may include additional parallel photoresist lines **142** separated by third trenches **144**. The additional parallel photoresist lines **142** may be formed of and include a conventional photoresist (e.g., an ArF sensitive photoresist, a KrF sensitive photoresist, etc.) that is the same as or different than that of the parallel photoresist lines **116** of the patterned photoresist material **114**, previously described with respect to FIG. **1**. The additional parallel photoresist lines **142** may have substantially similar dimensions and spacing as the parallel photoresist lines **116**, except oriented in a direction substantially perpendicular to that of the parallel features **130** (FIG. **4**) of the intermediate template structure **128** (i.e., perpendicular to the direction of the parallel photoresist lines **116**). For example, each of the additional parallel photoresist lines **142** may have a width W_3, thickness T_4, and length (not shown) substantially the same as the width W_1, the thickness T_2, and the length (not shown) of the parallel photoresist lines **116**, respectively. In additional embodiments, at least one of the thickness T_4 and the length of each of the additional parallel photoresist lines **142** may be different than at least one of the thickness T_2 and the length of the parallel photoresist lines **116**. The additional parallel photoresist lines **142** may be regularly spaced by a distance D_3 that is substantially the same as the distance D_1 between each of the parallel photoresist lines **116**. A pitch P_3 between centerlines C_3 of adjacent photoresist lines of the another patterned photoresist material **140** may be substantially the same as the pitch P_1 between the centerlines C_1 of the adjacent photoresist lines of the patterned photoresist material **114**. In some embodiments, the width W_3 of each of the additional parallel photoresist lines **142** is about 50 nm, the distance D_3 between adjacent additional parallel photoresist lines is about 70 nm, and the pitch P_3 between the centerlines C_3 of adjacent additional parallel photoresist lines is about 120 nm. The another patterned photoresist material **140** may be formed using conventional processes, such as those previously described in relation to forming the patterned photoresist material **114**.

Referring to next to FIG. **6**, the another patterned photoresist material **140** (FIG. **5**) may be used to form another patterned spacer material **146** including additional parallel spacers **148** separated by fourth trenches **150**. The another patterned spacer material **146** may define a second pattern **152** to be transferred to the intermediate template structure **128** (FIG. **4**), as described in further detail below. Each of the additional parallel spacers **148** may be formed of and include a material suitable for use as a mask for selectively removing (e.g., etching) portions of the additional template masking materials **134** and the intermediate template structure **128**. The material of the additional parallel spacers **148** may be the same as or different than the material of the parallel spacers **122** of the patterned spacer material **120**, previously described with respect to FIG. **2**. In some embodiments, each of the additional parallel spacers **148** is formed of and includes a silicon oxide.

The dimensions and spacing of the additional parallel spacers **148** may be selected to provide desired dimensions and spacing for features of a template structure to be formed using the another patterned spacer material **146**, as described in further detail below. The additional parallel spacers **148** may have substantially similar dimensions and spacing as the parallel spacers **122** of the patterned spacer material **120**, except oriented in a direction substantially perpendicular to that of the parallel features **130** (FIG. **4**) of the intermediate template structure **128** (i.e., perpendicular to the direction of the parallel spacers **122**). For example, each of the additional parallel spacers **148** may have a width W_4, thickness T_5, and length (not shown) substantially the same as the width W_2, the thickness T_3, and the length (not shown) of the parallel spacers **122**, respectively. Accordingly, the width W_4 of each of the additional parallel spacers **148** may be within a range of from about 20 percent to about 40 percent of a target pitch between adjacent openings of the rectilinear array of openings to be formed using the template structure, such as from about 20 percent to about 30 percent of the target pitch. In further embodiments, at least one of the thickness T_5 and the length of the each of the additional parallel spacers **148** may be different than at least one of the thickness T_3 and the length of the parallel spacers **122**. In addition, the additional parallel spacers **148** may be regularly spaced by a distance D_4 (i.e., equal to the width W_3 of each of the additional parallel photoresist lines **142**), that is substantially the same as the distance D_2 between each of the parallel spacers **122**. Accordingly, the distance D_4 between adjacent additional parallel spacers **148** may be within a range of from about 180 percent to about 160 percent of the target pitch between adjacent openings of the rectilinear array of openings to be formed using the template structure, such as from about 180 percent to about 170 percent of the target pitch. A pitch P_4 between centerlines C_4 of adjacent additional parallel spacers of the another patterned spacer material **146** may be substantially the same as the pitch P_2 between the centerlines C_2 of the adjacent parallel spacers of the patterned spacer material **120** (i.e., equal to about half of the pitch P_3 between centerlines C_3 of adjacent additional parallel photoresist lines of the additional parallel photoresist lines **142**). Accordingly, the pitch P_4 between adjacent additional parallel spacers of the another patterned spacer material **146** may be equal to about two times (2×) the target pitch between adjacent openings of the rectilinear array of openings to be formed using the template structure.

By way of non-limiting example, if a target pitch between adjacent openings of the rectilinear array of openings to be formed is about 30 nm, the width W_4 of each of the additional parallel spacers **148** may be within a range of from about 6 nm to about 12 nm, the distance D_4 between adjacent additional parallel spacers of the another patterned spacer material **146** may be within a range of from about 54 nm and about 48 nm, and the pitch P_4 between centerlines C_4 of adjacent additional parallel spacers of the another patterned spacer material **146** may be about 60 nm. In some embodiments, the width W_4 of each of the additional parallel spacers **148** is about 10 nm, the distance D_4 between adjacent additional parallel spacers of the another patterned spacer material **146** is about 50 nm, and the pitch P_4 between adjacent parallel spacers of the another patterned spacer material **146** is about 60 nm. The another patterned spacer material **146** may be formed using processes substantially similar to those previously described with respect to forming the patterned spacer material **120**.

Referring to FIGS. **7A** and **7B**, the first pattern **152** defined by the another patterned spacer material **146** (FIG. **6**) may be transferred or extended into the intermediate template structure **128** (FIG. **4**) to form a template structure **154**. The template structure **154** may include parallel features **130'** (described in more detail below), additional parallel features **156**, and elevated pillars **158**. The parallel features **130'** may intersect with the additional parallel features **156** to at least partially define wells **160**. The elevated pillars **158** may protrude from the locations where the parallel features **130** and the additional parallel features **156** intersect. A height H_3 of the elevated pillars **158** may be equal to the difference between a height H_4 of each of the parallel features **130** and the additional parallel features **156** and the thickness T_1 of the template material **106** (FIGS. **1** and **2**). In some embodiments, the height H_3 of the elevated pillars **158** is about 40 nm.

The parallel features **130'** may be substantially similar (e.g., in terms of dimensions and spacing) to the parallel features **130** of the intermediate template structure **128** previously described with reference to FIG. **4**, except that, as a result of extending the second pattern **152** into the intermediate template structure **128**, the parallel features **130'** may be formed from what used to be portions of the base **132** underlying the parallel features **130**. Thus, as shown in FIG. **7**B, the parallel features **130'** of the template structure **154** may have substantially the same width W_2, length (not numbered), and pitch P_2 as the parallel features **130** of the intermediate template structure **128** (FIG. **4**).

The additional parallel features **156** may have substantially the same width W_4, length (not shown), and pitch P_4 as each of the additional parallel spacers **148** (FIG. **6**). The additional parallel features **156** may also have substantially the same dimensions and spacing as the parallel features **130'**, except oriented in a direction substantially perpendicular to that of the parallel features **130'**. For example, referring to FIG. **7**B, the width W_4 of each of the additional parallel features **156** may be substantially the same as the width W_2 of each of the parallel features **130'**, the distance D_4 between adjacent additional parallel features of the additional parallel features **156** may be substantially the same as the distance D_2 between adjacent parallel features of the parallel features **130'**, and the pitch P_4 between centerlines C_4 of adjacent additional parallel features of the additional parallel features **156** may be substantially the same as the pitch P_2 between centerlines C_2 of adjacent parallel features of the parallel features **130**. Thus, the template structure **154** may include intersecting parallel features (i.e., the parallel features **130'**, and the additional parallel features **156**) defining substantially rectangular (e.g., square) wells. In addition, as illustrated in FIG. **7**A, each of the additional parallel features **156** and the parallel features **130'** may have substantially the same height H_3.

Since the parallel features **130'** and the additional parallel features **156** have substantially the same dimensions and spacing as the parallel spacers **122** and the additional parallel spacers **148**, the width W_2 of each of the parallel features **130'** and the width W_4 of each of the additional parallel features **156** may both be within a range of from about 20 percent to about 40 percent of a target pitch between adjacent openings of a rectilinear array of openings to be formed using the template structure **154**, such as from about 20 percent to about 30 percent of the target pitch. In addition the distance D_2 between each of the parallel spacers **122** and the distance D_4 between of the additional parallel spacers **148** may be within a range of from about 180 percent to about 160 percent of the target pitch between adjacent openings of the rectilinear array of openings to be formed using the template structure **154**, such as from about 180 percent to about 170 percent of the target pitch. Further, the pitch P_2 between centerlines C_2 of adjacent parallel features of the parallel features **130'** and the pitch P_4 between centerlines C_4 of adjacent additional parallel features of the additional parallel features **156** may both be about two times (2×) the target pitch between adjacent openings of the rectilinear array of openings. Still further, the height H_3 of each of the parallel features **130'** and the additional parallel features **156** may be within a range of from about one-half (½) the target pitch between adjacent openings of the rectilinear array of openings and about three times (3×) the target pitch between adjacent openings of the rectilinear array of openings, such as from about one times (1×) the target pitch and about two times (2×) the target pitch.

By way of non-limiting example, if a target pitch between adjacent openings of the rectilinear array of openings to be formed is about 30 nm, the width W_2 of each of the parallel features **130'** and the width W_4 of each of the additional parallel features **156** may be within a range of from about 6 nm to about 12 nm, the distance D_2 between adjacent parallel features of the parallel features **130'** and the distance D_4 between adjacent additional parallel features of the additional parallel features **156** may both be within a range of from about 54 nm and about 48 nm, the pitch P_2 between centerlines C_2 of adjacent parallel features of the parallel features **130'** and the pitch P_4 between centerlines C_4 of adjacent additional parallel features of the additional parallel features **156** may both be about 60 nm, and the height H_3 of each of the parallel features **130'** and the additional parallel features **156** may be within a range of from about is about 15 nm to about 90 nm. In some embodiments, the width W_2 of each of the parallel features **130'** and the width W_4 of each of the additional parallel features **156** are both about 10 nm, the distance D_2 between adjacent parallel features of the parallel features **130'** and the distance D_4 between adjacent additional parallel features of the additional parallel features **156** are both about 50 nm, the pitch P_2 between centerlines C_2 of adjacent parallel features of the parallel features **130'** and the pitch P_4 between centerlines C_4 of adjacent additional parallel features of the additional parallel features **156** are both about 60 nm, and the height H_3 of each of the parallel features **130'** and the additional parallel features **156** is about 35 nm.

As depicted in FIGS. **7**A and **7**B, the parallel features **130'** and the additional parallel features **156** may define sidewalls **162** of each the wells **160**, and the substrate masking material **104** may define a floor **164** of each of the wells **160**. Thus, if the parallel features **130'** and the additional parallel features **156** have substantially the same dimensions and spacing, each of the wells **160** may have substantially the same shape (e.g., substantially rectangular, such as substantially square), dimensions, and spacing. In some embodiments, each of the wells **160** has a square lateral cross-sectional shape, a lateral cross-sectional area of about 2500 nm^2, a height of about 35 nm, and is spaced apart from an adjacent well by about 10 nm.

Referring collectively to FIGS. **4**, **6**, and **7**A, to form the template structure **154**, the additional parallel spacers **148** of the another patterned spacer material **146** may be used as a mask for at least one etching process (e.g., an anisotropic etching process) to remove unmasked portions (e.g., portions not underlying the additional parallel spacers **148**) of each of the additional template masking materials **134** and the intermediate template structure **128** (FIG. **4**). The unmasked portions of the additional template masking materials **134** may be completely removed, and the unmasked portions of the intermediate template structure **128** may be partially removed. The etching process may, for example, uniformly remove unmasked portions of the intermediate template structure **128** to completely remove unmasked portions of the base **132** not underlying the parallel features **130** (FIG. **4**) and to transfer the dimensions of the parallel features **130** into the unmasked portions of the base **132** underlying the parallel features **130** (e.g., to form the parallel features **130'** of the template structure **154**). In further embodiments, depending on the conditions (e.g., time, chemistries, etc.) of the etching process, the height H_1 of the parallel features **130** of the intermediate template structure **128** may be different than (e.g., larger than) the height H_3 of the parallel features **130'** of the template structure **154**. Remaining portions of the additional parallel spacers **148** and the additional template masking materials **134** may then be selectively removed relative to the template structure **154**.

Referring to FIGS. **8**A and **8**B, a neutral wetting material **166** may be formed over the substrate masking material **104** defining the floor **164** of each of the wells **160**. The neutral wetting material **166** may be a material that has exhibits equal affinity for different polymer blocks (and any corresponding homopolymers, if present) of a block copolymer material to be deposited in the wells **160**. Thus, the neutral wetting material **166** may not be preferential (e.g., selective) to any polymer block (or homopolymer, if present) of a block copolymer material. The neutral wetting material **166** may, for example, be a neutral wetting carbon material, or a neutral wetting polymer. As a non-limiting example, if the block copolymer material to be deposited in the wells **160** is PS-b-PMMA, the neutral wetting material **166** may be a random PS:PMMA copolymer material (P(S-r-MMA)), a benzocyclobutene (BCP)- or azidomethylstyrene (AMS)-functionalized random copolymer of styrene and methyl methacrylate (e.g., P(S-r-MMA-r-BCP)), a hydroxyl functionalized random copolymer of styrene and methyl methacrylate (e.g., a 2-hydroxyethyl methacrylate (HEMA) functionalized random copolymer of styrene and methyl methacrylate (P(S-r-MMA-r-HEMA))), or a neutral wetting carbon material. In some embodiments, the neutral wetting material **166** is a neutral wetting carbon material. The neutral wetting material **166** may partially fill each of the wells **160**. The neutral wetting material **166** may be formed at any suitable thickness facilitating the formation of the self-assembled block copolymer material, such as a thickness within a range of from about 5 nm to about 10 nm.

The neutral wetting material **166** may be formed using conventional processes (e.g., a PVD process, a CVD process, an ALD process, or a spin-coating process), which are not described in detail herein. By way of non-limiting example, if the neutral wetting material **166** is a neutral wetting carbon material, the neutral wetting carbon material may be deposited in the wells **160** by a CVD process. As another non-limiting example, if the neutral wetting material **166** is a neutral wetting random copolymer material, the neutral wetting random copolymer material may be spin-coated into the wells **160** and cross-linked (e.g., by way of at least one of thermal-processing and photo-processing). After forming the neutral wetting material **166** on the floor **164** of the wells **160**, portions of the neutral wetting material **166** present on surfaces of the template structure **154** (e.g., surfaces of the parallel features **130'**, the additional parallel features **156**, and the elevated pillars **158** not proximate the substrate masking material **104**) may be removed.

In additional embodiments, the neutral wetting material **166** may be formed on the substrate masking material **104** prior to forming the template structure **154**. For example, the neutral wetting material **166** may be formed between the substrate masking material **104** and the template material **106** (FIG. **1**), and then the template structure **154** may be formed as previously described with reference to FIGS. **1** through **7**B (i.e., such that the template structure **154** is formed over the neutral wetting material **166**, and such that the neutral wetting material **166** defines the floor **164** of each of the wells **160**).

Referring next to FIGS. **9**A and **9**B, a block copolymer material **168** may be formed (e.g., deposited) in each of the wells **160**. As used herein, the term "block copolymer material" means and includes a material including at least one block copolymer. In turn, as used herein, the term "block copolymer" means and includes a polymer including two or more polymer blocks covalently bound to one or more polymer blocks of unlike type. The block copolymer material may also include at least one homopolymer of the same polymer type as a polymer block of the block copolymer included therein. As used herein, the term "homopolymer" means and include a polymer including a single type of repeat unit (e.g., a single repeating monomer). For example, the block copolymer material **168** may be a self-assembling (SA) block copolymer (e.g., an SA diblock copolymer, an SA triblock copolymer, etc.), or may be a blend of an SA block copolymer and at least one homopolymer of the same polymer type as a polymer block of the SA block copolymer. Suitable SA block copolymers may include, but are not limited to, PS-b-PMMA, PS-b-PDMS, polystyrene-block-polyvinylpyridine (PS-b-PVP), polystyrene-block-polyisoprene (PS-b-PI), polystyrene-block-polybutadiene (PS-b-PB), polystyrene-block-polylactide (PS-b-PA), polyethyleneoxide-block-polyisoprene (PEO-b-PI), polyethyleneoxide-block-polybutadiene (PEO-b-PB), polyethyleneoxide-block-polymethylmethacrylate (PEO-b-PMMA), polyethyleneoxide-block-polystyrene (PEO-b-PS), polybutadiene-block-polyvinylpyridine (PB-b-PVP), polyisoprene-block-polymethylmethacrylate (PI-b-PMMA). In some embodiments, the block copolymer material **168** is PS-b-PMMA. In additional embodiments, the block copolymer material **168** is PS-b-PDMS.

The block copolymer material **168** may have an SA block copolymer chain length and volumetric ratio of constituent polymers (i.e., polymer blocks of the SA block copolymer, and, if present, any homopolymers) facilitating the formation of a rectangular (e.g., square) array of cylindrical domains of a first polymer within a matrix domain of a second polymer in each of the wells **160**, as described in further detail below. For example, if the block copolymer material **168** is an SA diblock copolymer, a first polymer block to be self-assembled into the cylindrical domains may constitute from about 20 percent to about 40 percent of the total volume of the SA diblock copolymer, and a second polymer block to be self-assembled into the matrix domain may constitute a remaining percentage of the total volume of the SA diblock copolymer (e.g., from about 80 percent to about 60 percent of the total volume of the SA diblock copolymer). If the block copolymer material **168** is a blend of an SA block copolymer and at least one homopolymer, the at least one homopolymer may constitute from about 0.1 percent to about 40 percent of the total volume of the blend. In some embodiments, the block copolymer material **168** is a PS-b-PMMA copolymer including about 30 percent by volume PS and about 70 percent by volume PMMA. In additional embodiments, the block copolymer material **168** is a PS-b-PDMS diblock copolymer including about 30 percent by volume PS and about 70 percent by volume PDMS.

The block copolymer material **168** may substantially fill a remaining portion of each of the wells **160** (i.e., a portion of each of the wells **160** remaining after the formation of the neutral wetting material **166** therein). The sidewalls **162** of the wells **160** may be preferential wetting to one of the polymer blocks of the block copolymer material **168**. In addition, the block copolymer material **168** may be substantially contained within the wells **160** (i.e., less than or equal to a monolayer of the block copolymer material **168** may be located outside of the wells **160**, such as on the surfaces of the parallel features **130'**, the additional parallel features **156**, and the elevated pillars **158** outside of the wells **160**). In some embodiments, the block copolymer material **168** has a thickness within a range of about 25 nm to about 30 nm and is substantially contained in the wells **160**.

The block copolymer material **168** may be formed in each of the wells **160** using conventional processes (e.g., spin-coating, knife-coating, etc.), which are not described in detail herein. By way of non-limiting example, the block copolymer material **168** may be deposited into each of the wells **160** by spin-coating from a dilute solution of the block copolymer material **168** in an organic solvent (e.g., dichloroethane, toluene, etc.). The deposition process may be controlled so that capillary forces pull excess of the block copolymer material **168** (e.g., block copolymer material **168** deposited outside of the wells **160**) greater than a monolayer into the wells **160**.

Referring to FIGS. **10**A and **10**B, the block copolymer material **168** (FIGS. **9**A and **9**B) may be processed (e.g., annealed) to form a self-assembled block copolymer material **170** including a rectilinear array **172** of cylindrical domains **176** of a first polymer within a matrix domain **174** of a second polymer. The first polymer may correspond to a minority polymer of the block copolymer material **168** (e.g., a polymer, including a polymer block of an SA block copolymer and any corresponding homopolymer, present in a relatively lower amount), and the second polymer may correspond to a majority polymer of the block copolymer material **168** (e.g., another polymer, including another polymer block of an SA block copolymer and any corresponding homopolymer, present in a relatively greater amount). The sidewalls **162** of the wells **160** may be preferential wetting to the majority polymer of the block copolymer material **168**. For example, if the block copolymer material **168** is an SA block copolymer (e.g., an SA diblock copolymer), the first polymer may correspond to a minority polymer block of the SA block copolymer and the second polymer may correspond to a majority polymer block of the SA block copolymer. In some embodiments, the cylindrical domains **176** are formed of and include PS, and the matrix domain **174** is formed of and includes PMMA. In additional embodiments, the cylindrical domains **176** are formed of and include PS, and the matrix domain **174** is formed of and includes PDMS.

As shown in FIG. **10**B, the rectilinear array of cylindrical domains **172** may include rows of cylindrical domains **176** of the first polymer extending in an X direction and columns of the cylindrical domains **176** of the first polymer extending in a Y direction. The X direction may be substantially perpendicular to the Y direction. Each of the cylindrical domains **176** of the first polymer may have substantially the same width W_5 (i.e., diameter) and height H_5, and may be oriented perpendicular (i.e., surface normal) to the substrate **102**. In addition, within each row and each column, the cylindrical domains **176** of the first polymer may be substantially aligned and regularly spaced by a distance D_5. A pitch P_5 between centers C_5 of adjacent cylindrical domains (e.g., adjacent cylindrical domains of a particular row or a particular column) of the rectilinear array of cylindrical domains **172** may be substantially uniform throughout the self-assembled block copolymer material **170**.

By way of non-limiting example, the width W_5 of each of the cylindrical domains **176** of the first polymer may be equal to about one-fourth (¼) of the pitch (e.g., the pitch P_2, and the pitch P_4) between centerlines (e.g., the centerlines C_2, and the centerlines C_4) of adjacent features (e.g., adjacent parallel features of the parallel features **130'**, and adjacent additional parallel features of the additional parallel features **156**) of the template structure **154**. In addition, the height H_5 of each of the cylindrical domains **176** of the first polymer may be equal to the height of the block copolymer material **168** (FIGS. **9**A and **9**B). Furthermore, the pitch P_5 between centers C_5 of adjacent cylindrical domains may be equal to about one-half (½) of the pitch (e.g., the pitch P_2/and the pitch P_4) between centerlines (e.g., the centerlines C_2, and the centerlines P_4) of adjacent parallel features (e.g., adjacent parallel features of the parallel features **130'**, and adjacent additional parallel features of the additional parallel features **156**) of the template structure **154**. In some embodiments, the width W_5 of each of the cylindrical domains **176** is about 15 nm, the height H_5 of the cylindrical domains **176** is within a range of from about 25 nm to about 30 nm, and the pitch P_5 between centers C_5 of adjacent cylindrical domains of the cylindrical domains **176** is about 30 nm.

As illustrated in FIG. **10**B, the rectilinear array **172** of cylindrical domains **176** of the first polymer may be considered an aggregate of rectangular (e.g., square) arrays (not numbered) of the cylindrical domains **176** of the first polymer contained within the wells **160**. Namely, within each of the wells **160**, the dimensions and preferential wetting characteristics of the sidewalls **162** (i.e., as defined by parallel features **130'** and additional parallel features **156** of the template structure **154**) in combination with the characteristics of the neutral wetting material **166**, facilitates the formation of a rectangular array of the cylindrical domains **176** of the first polymer within the matrix domain **174** of the second polymer. Each rectangular array includes four of the cylindrical domains **176** of the first polymer having the dimensions and spacing previously described (e.g., width W_5, height H_5, and pitch P_5) in rectangular (e.g., square) registration. In turn, the dimensions and spacing of each of the parallel features **130'** and the additional parallel features **156** of the template structure **154** enables adjacent cylindrical domains **176** of adjacent rectangular arrays (i.e., in adjacent wells) to have the same alignment, dimensions, and spacing, resulting in the rectilinear array **172** of cylindrical domains **176**.

The self-assembled block copolymer material **170** may be formed using a annealing process. For example, the block copolymer material **168** may be thermally annealed at a temperature above the glass transition temperature of the polymer blocks and homopolymers (if any) of the block copolymer material **168** to effectuate separation and self-assembly according to the wetting characteristics of the wells **160** (e.g., the preferential wetting characteristics of the sidewalls **162**, and the neutral wetting characteristics of the neutral wetting material **166** on the floor **164**). As another example, the block copolymer material **168** may be solvent annealed by swelling the polymer blocks and homopolymers (if any) of the block copolymer material **168** with a solvent and then evaporating the solvent. In some embodiments, such as where the block copolymer material **168** is a PS-b-PMMA copolymer, the block copolymer material **168** is annealed at a temperature within a range of from about 180° C. to about 250° C. in a vacuum oven or under an inert atmosphere for a period of time within a range of from about 2 minutes to about 24 hours to form the self-assembled block copolymer material **170**.

Referring next to FIGS. **11**A and **11**B, the cylindrical domains **176** (FIGS. **10**A and **10**B) of the first polymer may be selectively removed to form a patterned polymer material **178** including the matrix domain **174** of the second polymer surrounding cylindrical openings **180**. The cylindrical openings **180** have substantially the same dimensions (e.g., width W_5, and height H_5), spacing (e.g., distance D_5, and pitch P_5), and alignment as the cylindrical domains **176** of the first polymer. The patterned polymer material **178** may thus define a rectilinear pattern **182** of cylindrical openings **180** (i.e., derived from and having substantially the same dimensions and spacing as the rectilinear array of cylindrical domains **172** of the first polymer) to be transferred to the substrate **102**, as described in further detail below.

The selective removal of the cylindrical domains **176** of the first polymer to form the patterned polymer material **178** may be performed using conventional processes, which are not described in detail herein. By way of non-limiting example, the cylindrical domains **176** of the first polymer may be removed using at least one of an oxygen plasma process and a chemical dissolution process (e.g., a process including irradiating the cylindrical domains **176** of the first polymer, ultrasonicating the self-assembled block copolymer material **170** in acetic acid, ultrasonicating the self-assembled block copolymer material **170** in deionized water, and rinsing the self-assembled block copolymer material **170** to remove the cylindrical domains **176** of the first polymer).

Referring next to FIGS. **12**A and **12**B, the rectilinear pattern **182** of cylindrical openings **180** defined by the patterned polymer material **178** may be transferred or extended into the substrate **102** (FIGS. **11**A and **11**B) to form a patterned substrate **184** including a rectilinear array **186** of openings **188**. The rectilinear array **186** may include rows of openings **188** extending in the X direction and columns of the openings **188** extending in the Y direction. The openings **188** may extend partially into the patterned substrate **184**, or may extend completely through the patterned substrate **184**. The openings **188** may have substantially the same width W_5 as the cylindrical openings **180** of the patterned polymer material **178** (i.e., the same width W_5 as the cylindrical domains **176** of the self-assembled block copolymer material **170**). In addition, within each row and each column, the openings **188** may be substantially aligned and may have the same pitch P_5 as the cylindrical openings **180** of the patterned polymer material **178** (i.e., the same pitch P_5 as the cylindrical domains **176** of the self-assembled block copolymer material **170**). In some embodiments, each of the openings **188** extends partially into the patterned substrate **184**, the width W_5 of each of the openings **188** is about 15 nm, and the pitch P_5 between adjacent openings **188** is about 30 nm.

To form the patterned substrate **184**, the matrix domain **174** of the patterned polymer material **178** may be used as a mask for at least one etching process (e.g., an anisotropic etching process, such as an reactive ion etching process) to substantially remove unmasked portions (e.g., portions not underlying the matrix domain **174**) of each of the substrate masking material **104** and the substrate **102**. The unmasked portions of the substrate masking material **104** may be completely removed, and the unmasked portions of the substrate **102** may be at least partially removed (i.e., may be partially removed, or may be completely removed). The etching process may, for example, extend the rectilinear pattern **182** of openings **180** partially through the substrate **102** to form the rectilinear array **186** of openings **188** of the patterned substrate **184**.

Accordingly, a method of forming a rectilinear array of openings in a substrate may comprise forming a template structure comprising a plurality of parallel features and a plurality of additional parallel features perpendicularly intersecting the plurality of additional parallel features of the plurality over a substrate to define wells, each of the plurality of parallel features having substantially the same dimensions and relative spacing as each of the plurality of additional parallel features. A block copolymer material may be formed in each of the wells. The block copolymer material may be processed to form a patterned polymer material defining a pattern of openings. The pattern of openings may be transferred to the substrate to form an array of openings in the substrate.

In addition, a method of forming a semiconductor device structure may comprise forming a template structure comprising intersecting features defining substantially rectangular wells over a substrate, each of the intersecting features having substantially the same dimensions and being preferential wetting to a polymer block of a self-assembling block copolymer. A neutral wetting material may be formed over a floor of each of the substantially rectangular wells. A block copolymer material comprising the self-assembling block copolymer may be formed over the neutral wetting material. The block copolymer material may be self-assembled to form an array of cylindrical domains of a first polymer within a matrix domain of a second polymer, the array of cylindrical domains of the first polymer exhibiting uniform pitch between substantially all adjacent cylindrical domains of the first polymer. The cylindrical domains of the first polymer may be selectively removed to define a pattern of cylindrical openings in the matrix domain of the second polymer. The pattern of cylindrical openings may be transferred to the substrate.

Following the formation of the patterned substrate **184**, remaining portions of the template structure **154** (e.g., the parallel features **130'**, the additional parallel features **156**, and the elevated pillars **158**), patterned polymer material **178** (e.g., the matrix domain **174**), and the substrate masking material **104** may be removed, as depicted in FIGS. **13**A and **13**B. These materials may be removed using conventional processes, such as conventional etching processes, which are not described in detail herein. The semiconductor device structure **100** including the patterned substrate **184** may then be subjected to additional processing, as desired. For example, the openings **188** in the substrate **102** may be at least partially filled with a material, such as a conductive material, to form contacts (e.g., bond pads). By utilizing the methods of the disclosure, the contacts may be closely packed and may have a uniform pitch between adjacent contacts.

Accordingly, a semiconductor device structure of the disclosure may comprise a substrate defining a rectilinear array of openings, each opening of the rectilinear array of openings having substantially the same width of less than or equal to about 25 nm, and adjacent openings of the rectilinear array of openings having substantially the same pitch of less than or equal to about 50 nm.

The methods of the disclosure provide an effective and reliable way to control the dimensions and spacing of the rectilinear array of openings **186** of the patterned substrate **184**. The methods facilitate simple and cost-effective formation of very small openings **188** (e.g., critical dimensions of less than or equal to about 30 nm) that are closely packed (e.g., a pitch of less than or equal to about 50 nm) and are substantially aligned in multiple directions (e.g., in the X and Y directions). The methods of the disclosure advantageously facilitate improved device performance, lower cost, increased miniaturization of components, and greater packaging density as compared to conventional methods of forming a contact array for a semiconductor device structure (e.g., a DRAM device structure).

While the disclosure is susceptible to various modifications and alternative forms, specific embodiments have been shown by way of example in the drawings and have been described in detail herein. However, the disclosure is not intended to be limited to the particular forms disclosed. Rather, the disclosure is to cover all modifications, equivalents, and alternatives falling within the scope of the disclosure as defined by the following appended claims and their legal equivalents.

What is claimed is:

1. A method of forming an array of openings in a substrate, comprising:

forming a template structure comprising a plurality of parallel features and a plurality of additional parallel features perpendicularly intersecting the plurality of additional parallel features over a substrate to define wells, each of the plurality of parallel features having substantially the same dimensions and relative spacing as each of the plurality of additional parallel features;

forming a block copolymer material in the wells;

processing the block copolymer material to form a patterned polymer material defining a pattern of openings; and

transferring the pattern of openings to the substrate to form an array of openings in the substrate.

2. The method of claim 1, wherein forming the template structure comprising a plurality of parallel features and a plurality of additional parallel features comprises forming each of the parallel features and each of the additional parallel features to have substantially the same width within a range of from about 20 percent to about 40 percent of a target pitch between adjacent openings of the array of openings.

3. The method of claim 1, wherein forming the template structure comprising a plurality of parallel features and a plurality of additional parallel features comprises:

forming the plurality of parallel features to exhibit a substantially uniform pitch between adjacent parallel features, the substantially uniform pitch equal to about two times a target pitch between adjacent openings of the array of openings; and

forming the plurality of the additional parallel features to exhibit another substantially uniform pitch between adjacent additional parallel features, the another substantially uniform pitch substantially the same as the substantially uniform pitch exhibited by the plurality of parallel features.

4. The method of claim 1, wherein forming the template structure comprising a plurality of parallel features and a plurality of additional parallel features comprises forming each of the parallel features and the additional parallel features to have substantially the same height within a range of from about one-half to about three times a target pitch between adjacent openings of the array of openings.

5. The method of claim 1, wherein forming the template structure comprising a plurality of parallel features and a plurality of additional parallel features comprises:

forming parallel spacers over a template material, each of the parallel spacers having substantially the same dimensions and spacing;

transferring a first pattern defined by the parallel spacers to the template material to form an intermediate template structure comprising initial parallel features protruding from a base;

forming additional parallel spacers over the intermediate template structure, the additional parallel spacers oriented in a direction substantially perpendicular to the parallel spacers and having substantially the same dimensions and spacing as the parallel spacers; and

transferring a second pattern defined by the additional parallel spacers to the intermediate template structure to form the template structure.

6. The method of claim 5, wherein forming parallel spacers over the template material comprises:

forming parallel photoresist lines exhibiting a first substantially uniform pitch between adjacent parallel photoresist lines, each of the parallel photoresist lines having substantially the same width and height;

forming a spacer material over the parallel photoresist lines; and

removing a portion of the spacer material to form the parallel spacers on sidewalls of the parallel photoresist lines, the parallel spacers exhibiting a second substantially uniform pitch between adjacent parallel spacers, the second substantially uniform pitch equal to about one-half the first substantially uniform pitch.

7. The method of claim 6, wherein forming additional parallel spacers over the intermediate template structure comprises:

removing materials remaining over the intermediate template structure after the formation thereof;

forming additional parallel photoresist lines over the intermediate template structure after removing materials remaining over the intermediate template structure, the additional parallel photoresist lines oriented in a direction substantially perpendicular to the parallel photoresist lines and having substantially the same dimensions and spacing as the parallel photoresist lines;

forming additional spacer material over the additional parallel photoresist lines; and

removing a portion of the additional spacer material to form the additional parallel spacers on sidewalls of the additional parallel photoresist lines.

8. The method of claim 5, wherein transferring the first pattern defined by the parallel spacers to the template material to form the intermediate template structure comprises extending the first pattern partially into the template material.

9. The method of claim 1, wherein forming the template structure comprising the plurality of parallel features and the plurality of additional parallel features comprises forming the template structure from a template material preferential wetting to a polymer block of the block copolymer material.

10. The method of claim 1, further comprising forming a neutral wetting material over floors of the wells prior to forming the block copolymer material in the wells.

11. The method of claim 1, wherein forming the block copolymer material in the wells comprises formulating the block copolymer material to have a block copolymer chain length and volumetric ratio of constituent polymers facilitating the formation of a rectangular array of cylindrical domains of a first polymer within a matrix domain of a second polymer within the wells during the processing of the block copolymer material.

12. The method of claim 1, wherein forming the block copolymer material in the wells comprises depositing a self-assembling diblock copolymer comprising:

a first polymer block comprising from about 20 percent to about 40 percent of a total volume of the self-assembling diblock copolymer; and

a second polymer block comprising a remaining percentage of the total volume of the self-assembling diblock copolymer.

13. The method of claim 1, wherein processing the block copolymer material to form a patterned polymer material defining a pattern of openings comprises:

annealing the block copolymer material to form a self-assembled block copolymer material comprising an array of cylindrical domains of a first polymer within a matrix domain of a second polymer; and

selectively removing the cylindrical domains of the first polymer to form the patterned polymer material.

14. A method of forming a semiconductor device structure, comprising:

forming a template structure comprising intersecting features defining substantially rectangular wells over a substrate, each of the intersecting features having substantially the same dimensions and being preferential wetting to a polymer block of a self-assembling block copolymer;

forming a neutral wetting material over a floor of each of the substantially rectangular wells;

forming a block copolymer material comprising the self-assembling block copolymer over the neutral wetting material;

self-assembling the block copolymer material to form an array of cylindrical domains of a first polymer within a matrix domain of a second polymer, the array of cylindrical domains of the first polymer exhibiting uniform pitch between substantially all adjacent cylindrical domains of the first polymer;

selectively removing the cylindrical domains of the first polymer to define a pattern of cylindrical openings in the matrix domain of the second polymer; and

transferring the pattern of cylindrical openings to the substrate.

15. The method of claim **14**, wherein forming the template structure comprising intersecting features defining substantially rectangular wells comprises forming the intersecting features to have the same width within a range of from about 6 nm to about 12 nm.

16. The method of claim **14**, wherein forming the template structure comprising intersecting features defining substantially rectangular wells comprises forming the intersecting features to exhibit a substantially uniform pitch of less than or equal to about 60 nm between adjacent parallel features thereof.

17. The method of claim **14**, wherein the self-assembling block copolymer comprises PS-b-PMMA or PS-b-PDMS.

18. The method of claim **14**, wherein forming the block copolymer material comprising the self-assembling block copolymer over the neutral wetting material comprises depositing the block copolymer material to substantially fill a remaining space within each of the substantially rectangular wells.

19. The method of claim **14**, wherein self-assembling the block copolymer material to form an array of cylindrical domains of a first polymer within a matrix domain of a second polymer comprises annealing the block copolymer material to form an array of four of the cylindrical domains of the first polymer within the matrix domain of the second polymer in each of the substantially rectangular wells.

20. The method of claim **14**, wherein transferring the pattern of cylindrical openings to the substrate comprises etching the substrate using the matrix domain of the second polymer as an etch mask to form an array of openings in the substrate.

21. The method of claim **20**, further comprising at least partially filling the array of openings with material.

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