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Chemically Amplified Deep UV Resists for Micromachining Using Electron Beam Lithography and Dry Etching

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Our paper focuses on the development of micro-, submicro-, and nano-structuring processes in microtechnology using single-layer multi-component chemically amplified resists (CARs) in connection with direct-write electron-beam lithography (EBL) and reactive ion etching (RIE). This technique offers the possibility of transferring 3-D structures deeply into the substrate with nearly vertical sidewalls, a high aspect ratio and good critical-dimension (CD) control.

1. Introduction

The reduction of feature sizes places new demands on the entire microtechnological process. To meet the advanced CD uniformity and resolution requirements in microfabrication, advanced high-resolution lithography and simple methods to perform conformal deep structure transfer into the substrate are required. The fabrication of microdevices was traditionally accomplished using conventional photolithography with wet chemical etching. However, the parameters of these techniques are difficult to be precisely controlled.

For ever-increasing device complexity, lithography and dry etching are the most critical processes; for both, the resist used is the most critical factor. The multilayer resist process includes many complicated processing steps and therefore it is not considered for practical EBL. It has been shown recently[1] that CARs can be used in EBL as well as in the deep-UV exposure mode. An effective micromechanical structure needs a pattern transfer with vertical sidewalls and minimum CD loss. The most critical factor in this is the 3-D shape of the relief structure. This applies to relatively thick resist layers as well. In this work, a new multicomponent Novolak-based CAR material (developed by HOECHST Corp.) and a recently developed non-Novolak-based CAR material (introduced by Olin Microelectronic Materials Corp.) were investigated in connection with direct-write EBL and RIE techniques and evaluated with regard to their possible application as masking material for micromachining.

2. Materials and Methods

Various CARs with high resolution, sensitivity and adequate plasma process compatibility have recently emerged. A comparison of the characteristic curves of CARs and the most conventional Polymethyl-methacrylate (PMMA) e-beam resist are shown in Fig. 1. The resist processes for characterization of lithographic parameters were optimalized for maximum CD-latitude with pre-exposure-, exposure-, and post-exposure processes (Table 1). The most obvious problems in items of the practical use of commercially available CARs in microlithography are not only in the discrepancies observed between the designed and obtained resist geometry caused by the scattering of electrons (proximity effect), but also in the instabilities in the delay times between the resist-handling process periods and the shelf-life of the resists. For positive CARs, formation of an airborne contaminated low-solubility surface layer causes the so-called "T-top" profiles, or "filling" and "bridging" effects.[2,3] In case of negative-tone CARs, the problems are connected with gel formation at the resist-substrate interface.[4,5] These effects strongly deteriorate the pattern profile.[6]

Because we are interested in dry etching directly through a single resist layer (without an additional top surface imaging resist) deeply into the substrate, thicker resist films with vertical sidewalls of pattern reliefs are required. This means that CD-control requires high conformity not only in the lateral, but also in the 3rd-vertical dimension. The quantitative evaluation of the performance of Novolak-based positive- (AZ PF514) and negative-tone (AZ PN114) CARs (HOECHST) in the EBL and RIE of Si, SiO_2, GaAs, Nb were described in our previous papers.[4,7,8] Recently introduced non-Novolak based CARs (CAMP6, ARCH, ARCH2 from Olin deep-UV family) have also indicated the suitability for masking during dry etch processes.[3,9,10] All experiments were carried out using fine-line shaped EBL (modified Carl-Zeiss e-beam pattern generator ZBA 10/1) and a commercial Oxford Instruments μ-80 RIE machine.

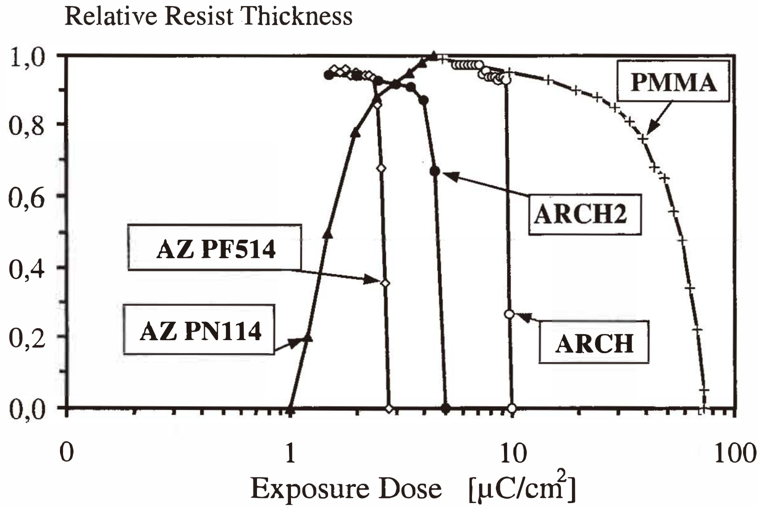

Fig. 1. Characteristic curves of CARs and PMMA.

Table 1
Process conditions of used resists.

Process step	Process conditions			
Resist	AZ PF514	AZ PN114	ARCH	ARCH2
Softbake (HP)	120°C/120 s	120°C/120 s	110°C/60 s	130°C/60 s
Developer*	AZ MIF 518	AZ MIF 518	OPD4262	OPD4262
Dev. time [s]	60	60	60	60
Q [μC/cm^2]**	2.8	1.2	10.0	5.0
PEB (HP)	80°C/60 s	100°C/300 s	110°C/60 s	110°C/60 s
PB: Oven/HP	80/90°C	80/120°C	–/120°C	–/110°C
Duration	30/5 min	30/5 min	–/1 min	–/1 min

*Development-immersion for 60 s
**Q = Large area sensitivity at 30 kV electrons
HP = Hot plate
PEB = Post exposure bake
PB = Post bake

3. Results and Discussion

EBL in a single-layer negative-tone AZ PN114 resist was demonstrated[4] on silicon (Fig. 2(a)) and GaAs (Fig. 2(b)) to realize (i) submicro- and nanometer quantum/cryoeletronic structures and (ii) silicon micromechanical parts (Fig. 3). The process optimization in the 1.1-μm-thick resist resulted in an increased resolution, better than 0.1 μm.

The patterned resist presents a good mask capability with the HBr/Cl_2 plasma chemistry. The single crystal silicon was etched 3 to 5 times faster than the AZ PN114 mask. The process quality was presented on a high-resolution nanostructure transferred into the silicon substrate with a < 10 nm CD-loss.[4] Figure 3(a) shows a part of silicon microreactor

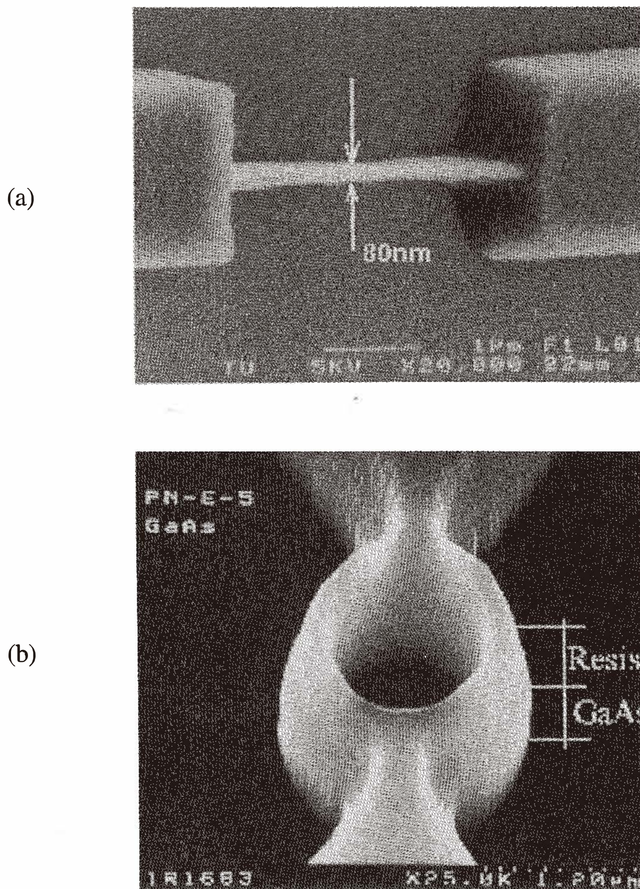

Fig. 2(a) Line-structure with 80 nm line width created in a 1-μm-thick AZ PN114 resist and etched ring-structure (diameter = 1.2 μm) through AZ PN114 into GaAs (Fig. 2(b)).

etched through SiO_2 mask silicon. The 2.6-μm-thick SiO_2 mask was directly etched through AZ PN114 resist by RIE with a CHF_3/Ar gas mixture at a pressure of 2.5 mTorr and 1.3 W/cm^2 power density. The best transfer capabilities into silicon through SiO_2 mask were obtained using a two-step process in RIE: (1) BCl_3 initialisation, which means surface scavenging. The surface of the silicon should be clear of native oxides, water, and other contaminants to avoid the "black silicon". The best scavenger for these types of contaminants is BCl_3 plasma. (2) The main-step etching of silicon in Cl_2/BCl_3 containing plasma. For micromechanical parts with a high aspect ratio, we also used $SF_6/O_2/CHF_3$/Ar-plasma

(a)

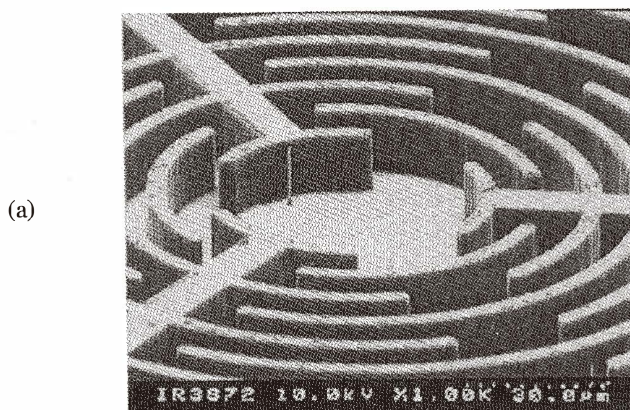

Fig. 3(a) Details of silicon microreactor for microreaction technology etched through the AZ PN114/SiO_2 mask in Cl_2/BCl_3 plasma.

(b)

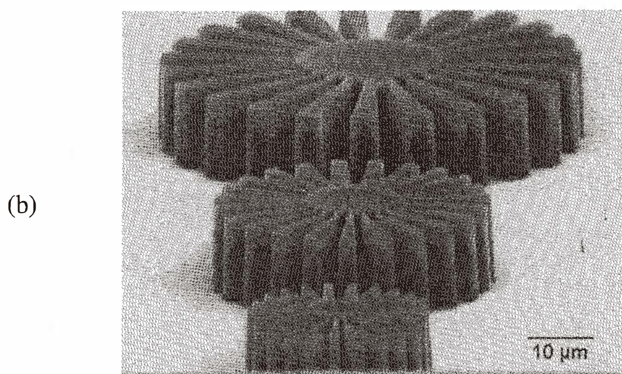

Fig. 3(b) High-aspect-ratio structures etched into silicon using $SF_6/O_2/CHF_3$/Ar plasma for plastic molding application.

(Fig. 3(b)). In this case, etch rate is much faster due to the high reaction probability of fluorine with silicon. In the RIE regime and at a very low rf power density of 0.05 W/cm^2 the etch rate in SF_6 plasma can be more than 1 μm/min.

Within the scope of this work we are focused on the reproducible RIE direct pattern transfer from the single-layer positive-tone AZ PF514 resist into the bulk and/or membrane silicon substrate. We carried out a number of experiments to find the masking capability of this resist in chlorine- and fluorine-containing plasma. Figure 4(a) shows a single-

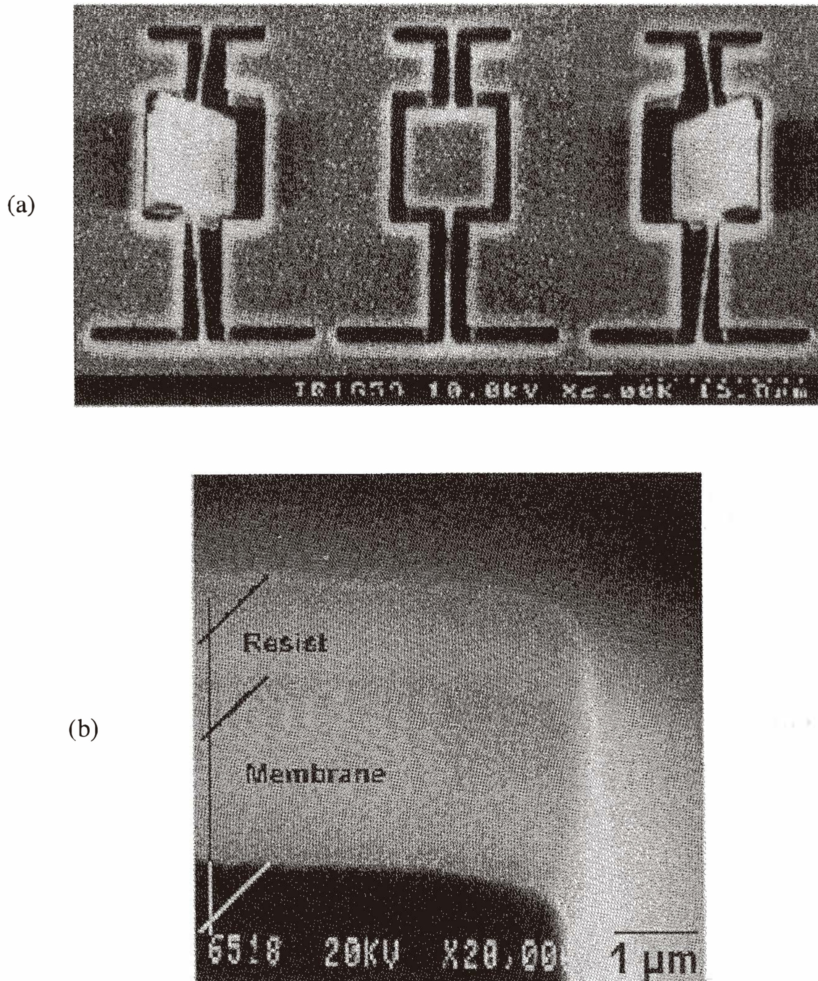

Fig. 4. Single movable micromechanical structure fabricated in the Si-membrane. Fig. 4(a) shows one moving sequence of the 10 × 10 μm^2 square mirror held by 0.3-μm-wide torsional Si-beams and Fig. 4(b) shows details of the etched membrane with remaining AZ PF514 resist.

crystalline silicon micromirror fabricated using the resist processing published in refs. (7) and (8), RIE and the technology based on sacrificial layers, as well as electrochemically stopped wet etching[12] (fully compatible steps with IC technology). In the first step, the 3.5-μm-thick silicon membrane was prepared using the etch stop at the p-n junction. The micromirror was defined using high-resolution EBL and etched using a high anisotropic bromine/chlorine RIE process. The best pattern transfer has been obtained for ion energy of 400 eV in a very low-pressure RIE mode. The etch selectivity with respect to silicon varied from 1 to 6, depending on the chemical and physical processes involved. Figure 4(b) shows the high quality of the remaining resist relief structure and the etching process. The fabricated $10 \times 10\ \mu m^2$ movable micromirrors are held by two 0.3-μm-wide and 1.5-μm-thick Si-membrane bridges. The developed simple micromechanical construction allows, for example, the use of the micromirror surface as a laser light deflector.[6]

The masking capability of positive-tone non-Novolak based ARCH and ARCH2 deep-UV resists (Olin Corp.) in fluorine- and chlorine-containing plasmas was examined.

For SiO_2 etching in CHF_3/Ar plasma, the etch selectivity of SiO_2 to ARCHs was ~5. Details of etched micromechanical structure (outer diameter = 10 μm) through 1-μm-thick ARCH resist into 3-μm-thick SiO_2 in CHF_3/Ar plasma is shown in Fig. 5.

Silicon trench etching was based on Cl_2/BCl_3 plasma chemistry implementing gas chopping[13] (BCl_3 flow on/off timing). A good etch selectivity of silicon to resist and a very smooth silicon base was achieved. The BCl_3 gas flow was switched on and off in periods of 200 s. In this way the formation of oxidized unsaturated halogenated film (micromasking) on the lower surfaces may be prevented. With such gas "chopping", etch rates of 200 and 30 nm/min for Si and ARCHs, respectively, were achieved; whereas in the case of permanently adding BCl_3 to Cl_2 the etch rate for Si was 180 nm/min and for ARCH

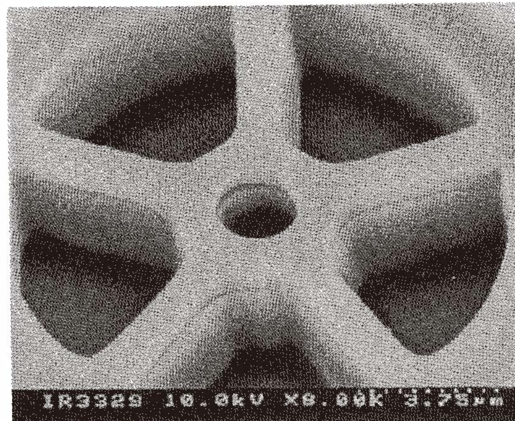

Fig. 5. Details of etched structure (outer diameter = 10 μm) through 1-μm-thick ARCH resist into 3-μm-thick SiO_2 in CHF_3/Ar plasma.

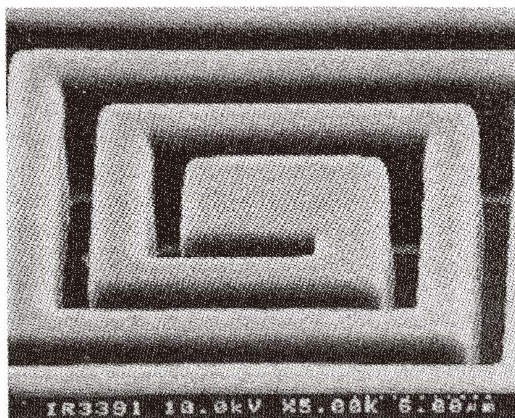

Fig. 6. Details of free-moving silicon microstructures fabricated using ARCH resist.

and ARCH2 it was 55 and 62 nm/min, respectively. Figure 6 shows a SEM of a stencil mask that was fabricated using the process described above to etch through a 6-μm-thick Si-membrane masked by ARCH resist.[10]

4. Conclusion

The possibility of fabricating deep-etched SiO_2 mask structures for silicon deep-trench etching through single layers of CARs for microsystem technology has been demonstrated. It was shown that under appropriate process conditions a high degree of pattern fidelity down to 0.5 μm is possible to transfer thick single-layer CARs using EBL and RIE.

Acknowledgements

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