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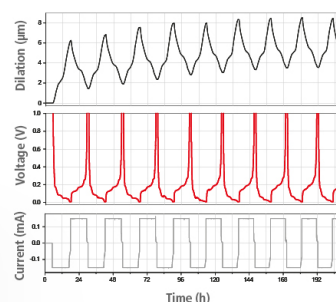
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A Flexible Multilayer Resist System Using Low Temperature Plasma-Deposited Silicon Nitride

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ABSTRACT

A three-layer resist system which uses positive photoresists for planarizing and imaging and an intermediate layer of plasma-deposited silicon nitride is described. The planarizing layer is 2 μm -thick Shipley AZ[®] 2430. The silicon nitride transfer layer is deposited at low temperature over hard-baked AZ 2430. Photon or electron imaging is done in a thin layer of resist spun on top of the transfer layer. The silicon nitride deposition process is described, and the properties of the resulting film are detailed. The planarizing photoresist is patterned by oxygen reactive ion etching. The vertical etch rate and the degree of isotropy are measured as a function of rf power and oxygen pressure. Controllable and reproducible undercut is achieved with this multilayer resist system. The resist profile is demonstrated to be suitable for lift-off applications or anisotropic etching of the substrate.

Multilayer resists have been employed by many to accomplish high resolution pattern transfer (1-6). The multilayer resists described here consist of three layers (Fig. 1). The bottom layer, the one covering the substrate, is a thick polymer layer which is used to planarize the topography of the substrate. A second layer, the transfer layer, separates the planarization layer from the imaging layer. The transfer layer keeps the imaging resist from mixing with the planarizing material, which may also be a photoresist. A thin imaging resist is then spun on top of the transfer layer. Because the resist is thin and flat, it is possible to achieve high resolution patterns even over complex topography. The imaging resist is exposed and developed and then used as a mask for etching the transfer layer. The etched transfer layer is subsequently used as a mask for reactive ion etching (RIE) of the planarizing layer. The transfer layer is usually an inorganic material which forms a nonerodible mask for oxygen RIE.

One advantage of multilayer resists is their flexibility. Because the planarizing resist is plasma or reactive ion etched, the sidewall profile can be accurately and reproducibly controlled. The thick resist may be vertically etched so the multilayer resist can be used as an etch mask for anisotropic etching of the substrate. The multilayer resist is a better mask for substrate etching than single-layer resist because the transfer layer, rather than an organic resist, is exposed to the plasma. A properly chosen transfer-layer material will stand up to plasma etching better than photoresist. Multilayer resists can also be processed so that the planarizing resist is undercut beneath the transfer layer. This profile is ideal for lift-off applications. The metal thickness is controlled by the thickness of the planarizing resist, making lift-off of thick metals possible. The pattern resolution is controlled independently by imaging in the thin top resist.

Additional flexibility is gained by being able to image in any type of resist. Photo-, E-beam, or x-ray resists can be used as the imaging resist without regard to future harsh processing steps. The resist is used only for lithography and as a mask for etching 1000Å of the transfer material. The imaging resist is usually re-

moved during reactive ion etching of the planarization layer. The multilayer resist system described here is being used in the application of same-level mixed lithography (7). In this application the resist is both optically and E-beam exposed. As a consequence, it is necessary to be able to optically align through the resist. For this reason, a transparent material is necessary for the transfer layer. Silicon nitride was chosen as the transfer material.

Silicon nitride is compatible with both silicon and GaAs technologies. It is currently used in both technologies as a final passivation layer because it serves as an excellent barrier to alkali diffusion. It also has application as an interlevel dielectric in multilayer metallization. Because it has such widespread use in the industry, processing with silicon nitride is routine, and its properties are well characterized. Silicon nitride can be plasma deposited at low temperatures uniformly across a wafer. It is also easily etched in fluorocarbon plasmas. This ease in handling makes silicon nitride a good choice for the transfer-layer material.

This paper will describe a multilayer resist system composed of plasma-deposited silicon nitride and positive photoresists. The processing steps will be described and the applications will be demonstrated.

Experiments

The multilayer resist (Fig. 1) was applied on 3 in. silicon wafers. The planarization layer was typically 1.7-2.0 μm of AZ[®] 2430,³ which was baked at 200°C for 30

³ AZ is a registered trademark of American Hoechst Corporation, Somerville, New Jersey, for their photoresist products.

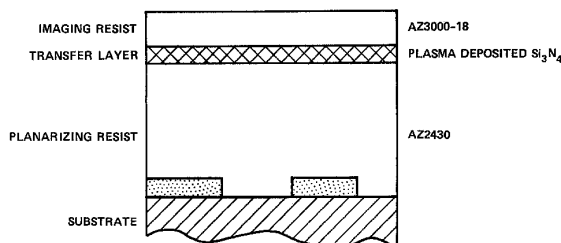


Fig. 1. Multilayer resist structure suitable for E-beam and optical exposure. Reactive ion etching of the planarizing resist leaves either vertical sidewalls or an undercut profile for lift-off applications.

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min in a convection oven. The silicon nitride transfer layer was applied on top of the hard-baked resist. Thickness of this layer was generally 0.1 μm .

The silicon nitride was plasma deposited in a modified Technics Planar Etch II reactor, as shown schematically in Fig. 2. The two electrodes, 20.3 cm in diam, were separated by 3.0 cm. Samples were uniformly spaced on the heated platen. The reactant gases entered the chamber through an annular plate, passed a diffusion ring, and flowed radially inward over the samples. The reaction by-products were exhausted through the center hole of the heated deposition plate.

Pressure and gas flow into the reactor were controlled independently. Reactant gases were controlled by a three-gas flow/ratio mass flow controller. This system provided closed-loop flow control and the capability of slaving any two of the gases to a third. Individual gas flows, as well as total-flow rate, were accurately maintained within the chamber. The desired process pressure was controlled independently by using a throttle valve and controller on the exhaust port. Depositions were made at a substrate temperature of 125°C. The platen was heated by a resistance heater sandwiched between the two aluminum plates comprising the platen. Temperature monitoring and control were accomplished by a thermocouple positioned between the plates.

The production of silicon nitride (Si_3N_4) was achieved by coreaction of nitrogen (N_2), ammonia (NH_3), and silane (SiH_4). Silane was introduced in an argon carrier gas, where the SiH_4/Ar ratio was 10/90. Ammonia was added because it is more easily dissociated than nitrogen. The larger concentration of free nitrogen atoms in the plasma resulted in silicon nitride films, which are less silicon rich than the films deposited from N_2/SiH_4 plasmas. The use of ammonia resulted in material having a more uniform index of refraction and thickness.

Under typical deposition conditions, input gas-flow rate ratios were $\text{N}_2/\text{NH}_3/\text{SiH}_4$ equal to 37/4.5/33.5 sccm. A total chamber pressure of 700 mtorr was maintained with the throttle valve. The plasma was sustained with 50W rf power applied to the top electrode from a 30 kHz generator. Under these conditions the deposition rate was 120 Å/min.

The properties of the silicon nitride film were characterized using a Rudolph AutoEl ellipsometer. The silicon nitride film was deposited directly on silicon substrates to determine the index of refraction and film thickness. The film thickness uniformity over a 3 in. wafer was determined by using the ellipsometer to

measure thickness at nine points on a wafer. The etch rate in Transene-buffered HF was measured by determining the film thickness before and after a timed etch. Etching in buffered HF was done for several different times, and the etch rates were calculated. The etch rate of the silicon nitride film in a CF_4/O_2 plasma could not be calculated in this way because the plasma changes the reflecting properties of the silicon nitride.

The imaging resist layer was spun on the silicon nitride transfer layer over HMDS adhesion promoter. Generally, 0.5 μm -thick AZ 2415 or Microposit 3000-18 was used for pattern definition. These resists could be either optically or E-beam exposed. After the pattern was developed in the imaging resist, it was used as a mask to etch the silicon nitride.

The silicon nitride was etched in a second Technics planar system. The etch gas was 97.5% CF_4 and 2.5% O_2 . The pressure was determined by the gas flow and maintained at 400 mtorr. The wafer was placed on a 20.3 cm grounded electrode, and etching was completed in 48s using 50W applied power. The wafers were given a 9s dip in Transene buffered HF before nitride etching. Following the nitride etch, the wafers were baked at 100°C for 1h.

Reactive ion etching of the planarization layer was done with 13.56 MHz rf power applied to the bottom electrode of a Plasma Therm PK 1241 reactor. The electrode was 25.4 cm in diam, and the chamber volume was 13.5 liters. The applied power was varied between 50 and 450W, while the gas pressure and flow rate were held constant.

The etch gas used was MOS purity oxygen from Matheson. The flow of gas into the chamber was controlled by mass flowmeters. The pressure was held constant by an automatic venetian-blind valve controlled by a capacitance manometer. Pressures between 5 and 100 mtorr were studied. All etching was done with both electrodes maintained at 40°C.

In order to determine the etch rate, the samples were etched for varying time periods such that none of the etches completely removed the resist. Measurements were made from SEM photos of the etch depth and the amount of undercut. Etch rates were calculated from these data. The average etch rate and the standard deviation from the mean are reported. The amount of resist undercut, as measured at the resist-nitride interface, divided by the etch depth for the same time period is defined as the degree of isotropy. The degree of isotropy is a quantitative measure of the resist profile.

Silicon Nitride

The silicon nitride film that was plasma deposited in the system described above had an index of refraction of 1.81 ± 0.02 . This should be compared to the index of refraction of stoichiometric Si_3N_4 , which is 1.98. The lower index of the film deposited in our system suggests that it is nitrogen-rich material. This material can be deposited with a thickness uniformity of better than 5% over the surface of the wafer and less than 3.5% between three 3 in. wafers in the same run. The material which is deposited is more chemically reactive than either thermally deposited silicon nitride or plasma-deposited nitride, which is deposited at a higher temperature. The material being described etches in Transene-buffered HF at 700 Å/min. For comparison, plasma nitride deposited at 250°C etches at 500 Å/min; the etch rate of material deposited at 325°C is 300 Å/min; 750°C thermal nitride etches at 100 Å/min in BHF. In a CF_4/O_2 plasma which is 2.5% O_2 , the etch rate of the 125°C plasma nitride is 1400 Å/min. The etch is nearly isotropic, but since only 1000Å of nitride is being defined, the pattern dimensions can be preserved by stopping the etch just as the endpoint is reached.

Prior to silicon nitride deposition, the planarizing resist was hard-baked in a convection oven where the

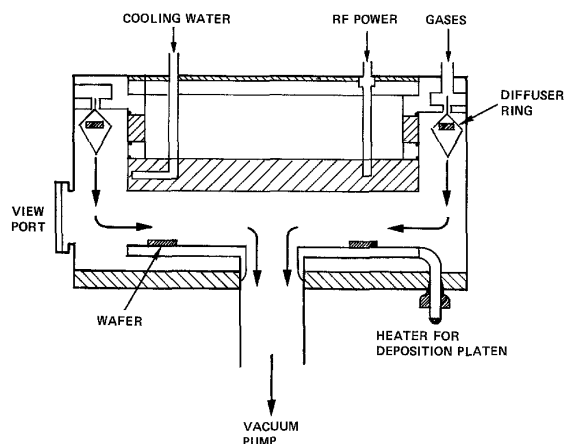


Fig. 2. Schematic drawing of planar reactor for the plasma deposition of silicon nitride. Material is deposited at 125°C by coreaction of N_2 , NH_3 , and SiH_4 with flows 37, 4.5, and 33.4 sccm, respectively, and a total pressure of 400 mtorr. The power is 50W.

minimum bake conditions were 200°C for 30 min. Baking at a temperature lower than 200°C resulted in a wrinkled photoresist layer with a textured silicon nitride layer on top of it. This is illustrated in Fig. 3. During plasma deposition of silicon nitride, the surface of the AZ 2430 planarizing resist was heated to temperatures greater than 125°C. At these temperatures, cellosolve acetate is volatilized from AZ resists and nitrogen gas is also released from decomposition of the photoactive compound (8). If the planarizing resist is not prebaked, these gases will be released during the silicon nitride deposition resulting in a wrinkling of both films. Shaw *et al.* (8) determined that for AZ 1350J photoresist, samples had to be heated to 160°C to remove all volatile components. For AZ 2430, samples must be heated to 200°C to prevent wrinkling.

Under some conditions, the silicon nitride film became completely resistant to a CF_4/O_2 plasma etch. It is believed that the silicon nitride surface becomes oxidized after it is deposited. This oxynitride surface layer can be removed in Transene-buffered HF. It was found that a 9s dip in buffered HF is the minimum time required to completely eliminate this unwanted film. After 9s the "oxide" layer was removed and almost all 1000Å of the silicon nitride film remained. The source of this oxide contamination is still being investigated.

After the CF_4/O_2 plasma etch of the nitride transfer layer, the wafer was baked at 100°C in a convection oven for 1h. The baking step was performed to prevent the nitride erosion seen in Fig. 4, which is a scanning electron micrograph of the multilayer resist after the planarization layer has been etched using the silicon nitride layer as a mask. This nitride erosion results in images substantially smaller than those originally defined in imaging resist, as well as ragged edges on those features. It is believed that the erosion is caused by the presence of fluorine in the plasma at the beginning of the oxygen RIE step. This fluorine may be trapped on the surface of the imaging resist during the CF_4/O_2 plasma etch of the nitride. Microprobe analysis has indicated the presence of fluorine

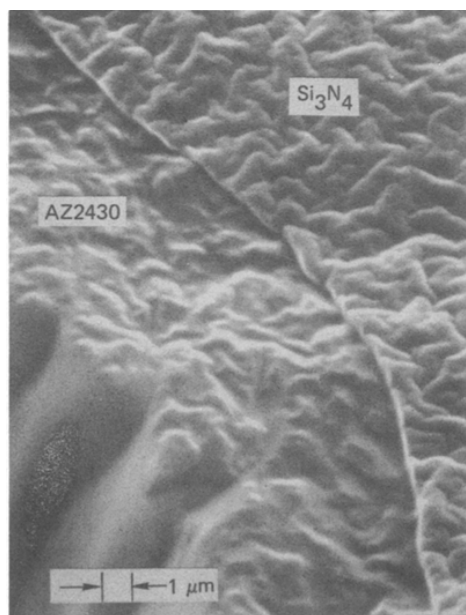


Fig. 3. SEM plots of silicon nitride transfer layer which was deposited on AZ 2430 which was not hard baked. Temperature increase during the deposition process causes both the resist and the nitride film to wrinkle.

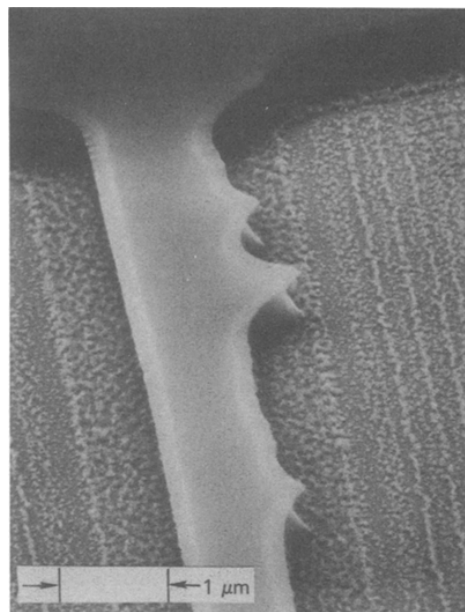


Fig. 4. Multilayer resist after nitride layer and planarization layer are etched. Ragged edges are caused by unwanted fluoride etching of the silicon nitride. The fluorine contamination can be removed by baking the wafer after the nitride etch.

in this layer, while Dobkin and Cantos (9) also found evidence for this in their work. Oxygen RIE removes the top imaging resist as well as the bottom planarizing resist, an interaction which releases the trapped fluorine to react with the silicon nitride transfer layer. The fluorine is only present at the beginning of the O_2 etch, because it is only released from the surface of the imaging resist.

The problem arises when the imaging resist does not have a square profile. Poor resist profiles are dome shaped, being thinner near the edges of the feature than in the middle. If the edges of the imaging resist are removed very early in the oxygen etch, the silicon nitride will be exposed to reactive fluorine. This is probably the cause of the nitride erosion. One solution to the problem would be to have resist profiles which do not have sloping walls, since this would assure that all fluorine is removed from the surface of the photoresist and pumped away before any silicon nitride is uncovered. An empirical solution to the problem has been to bake the sample before the oxygen RIE step is done. It is believed that the baking releases the fluorine from the surface of the photoresist; however, we have been unable to confirm this with a microprobe experiment because the fluorine signals are very small.

Reactive Ion Etching and Profile Control

Once the features were defined in the silicon nitride layer, it was used as a mask for etching the thick planarizing resist. This resist was etched in a low pressure oxygen plasma. The wafers were placed on the powered electrode so that they received high ion bombardment. Figure 5 shows the measured degree of isotropy as a function of chamber pressure and rf power. The degree of isotropy is a quantitative way to describe the profile of the etched resist and silicon nitride mask, and is defined as the lateral etch rate divided by the vertical etch rate. Figure 5 shows that power has very little effect on changing the degree of isotropy. Large variations in the degree of isotropy do occur when the pressure is varied. Completely anisotropic etching occurs only at pressures below 5 mtorr and powers greater than 150W. The dependence

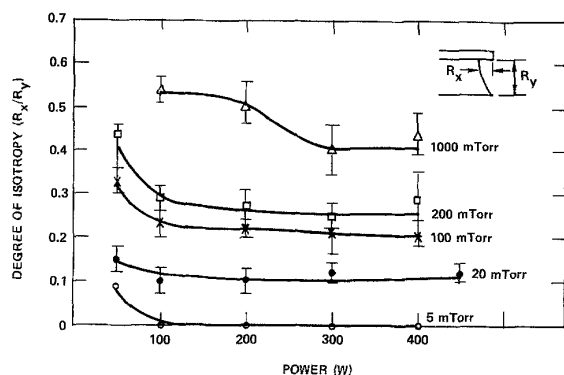


Fig. 5. Degree of isotropy of hard-baked AZ 2430 after oxygen RIE. The ratio of lateral to vertical etch rate is shown as a function of rf power for several system pressures.

of the degree of isotropy on oxygen pressure and rf power will be discussed further in another paper (10).

The vertical etch rate of the planarizing resist is plotted against power for constant pressure values in Fig. 6. Except for the data taken at 100 mtorr, the etch rate increases linearly with power input. At 100 mtorr, the etch rate increases with power, but not linearly. As the rf power input into the system increases over the range studied, the electrons in the plasma acquire a higher average energy. As the electron energy increases, the number of ionizing collisions increases (11). Ionization of the oxygen molecules produces positive ions, which are accelerated vertically toward the wafer by the sheath potential. Increasing the rf power increases both the number of positive ions and the sheath potential so that the vertical etch rate is seen to increase with the power.

The effect of varying the system pressure on the etch rate is more complicated. At low pressures (less than ~ 100 mtorr), the etch rate increases with increasing pressure because the number of reactive species increases with the increasing number of electron-molecule collisions. (There are more O_2 molecules available for collisions at higher pressures.) As the number of molecules increase with increasing pressure, the time between electron-molecule collisions decreases. This shortened time results in lower average electron energy because the electric field has less time to accelerate the electron before it collides (12). The lower average electron energy results in fewer

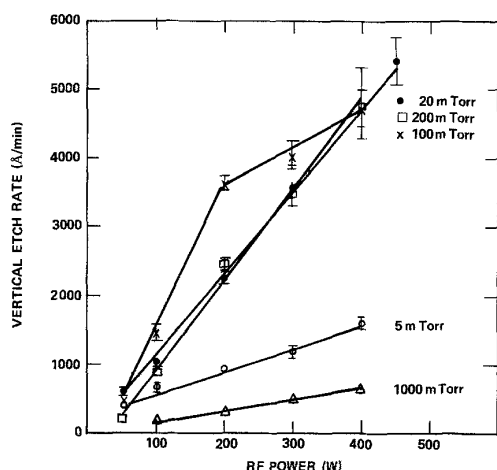


Fig. 6. Etch rates for hard-baked AZ 2430 in an oxygen plasma. The etch rates are given as a function of rf power for several system pressures.

collisions energetic enough to ionize the molecular oxygen. At pressures greater than ~ 100 mtorr, the number of ionizing collisions starts to decrease as the pressure is increased, as seen in Fig. 6.

Reactive ion-etch parameters can be chosen based on the information in Fig. 5 and 6. Gas pressure and rf power determine the degree of isotropy obtained in the planarizing resist profile. The etch rate data are used to determine the etch time to endpoint. Figure 7 shows the multilayer resist which has been defined anisotropically. The imaging resist layer is removed during the oxygen RIE so the SEM photograph only shows the etched transfer and planarization layers. The imaging resist, Microposit 3000-18, was exposed with electrons. By using electron beam lithography, features as small as $0.3 \mu\text{m}$ have been processed with this multilayer scheme. Etching beyond endpoint produces a film on the sidewalls of the planarizing resist on silicon substrates. It is believed that these films are similar to those described by Kinsbron (13). On silicon substrates, the sidewall film is probably some silicon-oxygen compound and is easily removed in buffered HF.

Figure 8 shows the multilayer resist processed with an undercut so it can be used for lift-off definition of metals. The degree of isotropy is 0.25, and $0.4 \mu\text{m}$ of a metal alloy has been deposited over the multilayer resist. The degree of isotropy is reproducible within the error bars shown in Fig. 5. This reproducibility leads to well-controlled lift-off profiles. The thick planarization layer makes it possible to define very tall features. The silicon nitride transfer layer has supported as much as a $1.5 \mu\text{m}$ layer of Ti/Au alloy without any signs of strain. After the metal has been deposited over the multilayer resist, the planarizing resist must be dissolved to carry away the excess metal. Resists baked at 200°C are not soluble in acetone, the usual lift-off solvent. A commercial epoxy remover, Uresolve Plus (Dynaloy, Incorporated), is suitable for removing the hard-baked resist in the final lift-off step. Uresolve Plus is strongly alkaline and is not suitable for lift-off directly on GaAs. Other, less caustic solvents are being sought for this application.

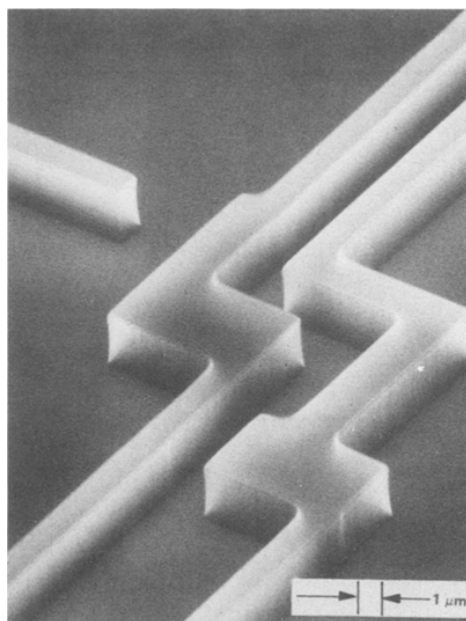


Fig. 7. Anisotropically etched AZ 2430 with a Si_3N_4 mask. The imaging resist which was removed in the oxygen RIE step was patterned using E-beam lithography.

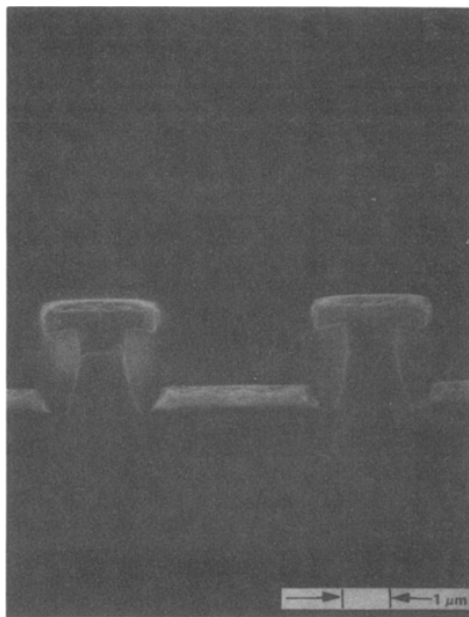


Fig. 8. Multilayer resist processed with an undercut suitable for lift-off metal deposition. $0.4\ \mu\text{m}$ of Ti/Au is deposited on the resist structure.

Summary

A very flexible multilayer resist system has been developed using positive resists and plasma-deposited silicon nitride. The low temperature plasma nitride can be uniformly deposited over the surface of the wafer, resulting in a three-layer system which is completely transparent, making optical alignment possible. The imaging resist can be either optically or E-beam exposed, and no charging occurs during the E-beam exposure.

Reactive ion etching of the planarizing resist produces controllable profiles. The profile can be varied from vertical wall to any degree of isotropy desired for a lift-off application. Characterization of the etch rate and degree of isotropy as a function of pressure and power has led to predictable and reproducible resist profiles.

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Effective Segregation Coefficient of Boron in Silicon Ingots Grown by the Czochralski and Bridgman Techniques

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ABSTRACT

Hall measurements and four-point probe resistivity measurements were used to determine the concentration profile of boron in doped semiconductor silicon ingots grown by Czochralski and Bridgman techniques. The concentration profiles were fitted to the normal segregation equation and the effective segregation coefficient, k_{eff} , was calculated. The average value of k_{eff} for boron was 0.786 ± 0.036 in Czochralski single crystals and 0.803 ± 0.036 in Bridgman polycrystals.

Silicon made by carbothermic reduction of silica in an arc furnace is becoming increasingly important as a source of low cost silicon for solar cells (1-3). The arc furnace-derived silicon normally contains both boron and phosphorus doping impurities which are difficult to assay reliably by chemical analysis. Multiple recrystallization of the arc furnace silicon and Hall measurements on the crystals thus obtained has been suggested as an accurate method of determining boron and phosphorus concentration in arc furnace silicon

(4). The method, however, requires an accurate knowledge of segregation coefficients for these impurities. This information is also necessary to estimate the extent of purification achievable by crystal growth.

An equilibrium distribution coefficient is based strictly on thermodynamic considerations. It is normally calculated from a phase diagram as the ratio of the slope of solidus to liquidus. However, in practice, this value of the distribution coefficient can be approached only at slow growth rates and for solidification from well stirred melts. Therefore, it is customary

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