

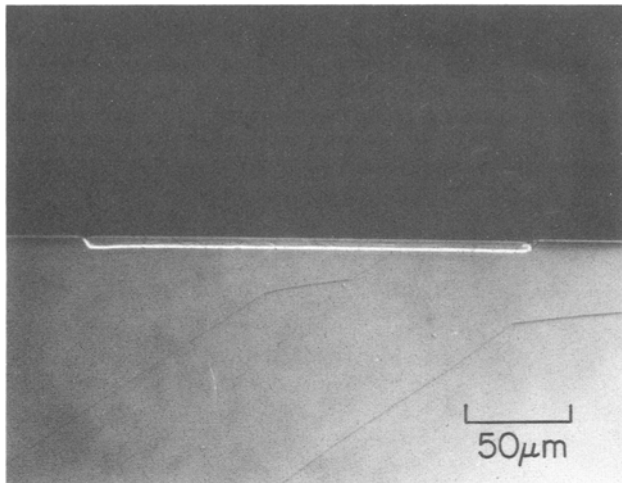


Fig. 9. Epitaxial layer without overgrowth at 8 A/cm² for 6 min. Well etched at 8 A/cm² for 3 min.

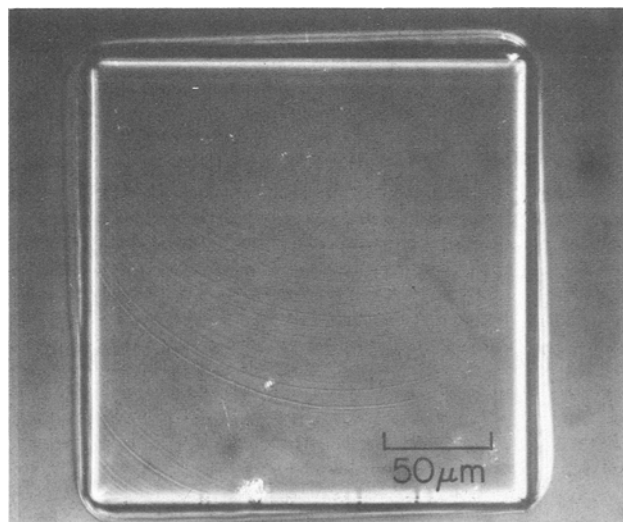


Fig. 10. Typical surface morphology of selectively grown epilayer

rections, a microorientation of the original window edges from the $\langle 110 \rangle$ directions causes the edges of the grown layers not to be exactly parallel to the edges of SiO₂-masked edges.

Although ion implantation is at present widely used for GaAs IC structures, the potential of preferential

epitaxial growth for this purpose does not appear to have been fully explored as yet.

Summary

It was shown that selective dissolution on GaAs windows can be successfully carried out and controlled by controlling the current density across the substrate-solution interface. Reversing the current polarity leads to electroepitaxial growth, which again can be controlled by controlling the current density. Both dissolution and growth are in fact linearly dependent on current density. Selective electroepitaxy (without overgrowth) is best carried out at relatively low current densities (less than about 15 A/cm²). The present results indicate that it might be worthwhile to pursue selective electroepitaxy in achieving IC structures.

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Optical Absorption of Thin SIPOS Films

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ABSTRACT

Optical techniques were used to extract refractive index and absorption coefficient from thin film transmittance and reflectance data for a family of CVD SIPOS films as-deposited and subsequent to a 1 hr 1000°C N₂ anneal. Optical measurements in the 0.5-2.5 eV range indicate a dependence of absorption on both oxygen content and annealing conditions.

SIPOS (semi-insulating polycrystalline silicon) is an acronym applied to a family of glasses whose composition can be written SiO_x ($x < 2$). The technological significance of these films has been demonstrated by

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Key words: amorphous films, silicon oxides, absorption.

their utilization as a passivation layer for high voltage power devices (1, 2) and as a field oxide for channel stopperless (MOS technologies) (3).

Investigations utilizing field effect conductance modulation and thermal activation of electrical conductivity (4) indicate that the mobility gap in these

films is a strong function of oxygen concentration. The discovery that with suitable annealing treatments SIPOS films can be doped n- and p-type in conjunction with the low interfacial recombination velocity of SIPOS/Si interfaces has led to the fabrication of SIPOS/Si heterojunction bipolar transistors (5, 6).

In general, the optical and electrical properties of materials are indirectly related through the density of states. Since optically active states are not necessarily those involved in electronic conduction, the "bandgaps" deduced from optical and electrical measurements cannot be expected to yield the same values; yet, a qualitative correlation between these quantities exists, and measurements of the optical absorption should indicate an absorption edge in these SIPOS films which displays a blue shift for higher oxygen concentrations.

Experimental Procedure

The films used in this study were deposited at 665°C on fused silica substrates in an rf heated, horizontal, atmospheric pressure, cold wall reactor. The silane and nitrogen carrier flows were held constant while the nitrous oxide flow rate was adjusted to vary the oxygen concentration. Table I lists the values for the various processing parameters.

After extracting total (specular and diffuse) transmittance and reflectance data using a Beckman DK-2 double beam spectrophotometer, the samples were annealed in a nitrogen ambient at 1000°C for 1 hr. Subsequent to optical measurements these annealed films were waxed and etched in a 20:1 HNO₃:NH₄F solution to produce a step suitable for mechanical step height measurements with a Tencor α -step.

Thin film analysis.—For absorptance and refractive index studies in the 0.5-2.5 eV region, the films used were in the 1-2 μ m thickness range. Thinner films would not yield useful information on the low energy absorption and the lack of a sufficient number of interference fringes would have compounded the difficulty in extracting the refractive index. Thicker films would yield transmittance values too small to be reliably distinguished from background noise. A single compromise thickness was chosen to cover the anticipated absorption edge.

Interference effects appear when the wavelength of the incident radiation is comparable to the film thickness. For shorter wavelengths, the increased absorption and the variations in the film thickness will damp the interference fringes, allowing simpler limiting forms for the transmittance and the reflectance to be used.

For the films used in this study, the wavelengths can be divided into three regions—long λ , negligible absorption, and dispersion; moderate λ , moderate absorption, small dispersion; short λ , strong absorption, and absence of interference patterns. The formulas for R and T , the reflectance and transmittance, in their full form do not lend to straight forward extraction of the real refractive index (n), the absorption coefficient (α), and the film thickness (d). In principle these three quantities can be uniquely determined from the experimental quantities R , T , λ , and the fringe order, but in practice, simplifying assumptions are usually applied.

In the low absorption regime where $\alpha d \ll 1$, the formula presented in Abeles (9) for a transmission ex-

tremum can be used to extract n , α , and d . Since the value of R at a reflectance minimum is small, and is comparable to the substrate back-reflectance, error introduced in the measurement is minimized by utilizing R values at reflectance maxima, i.e., the transmittance minima. If we let R_1 be the corresponding reflectance and T_1 the transmittance then

$$n^2 = n_s \left(\frac{1 + \sqrt{R_1}}{1 - \sqrt{R_1}} \right) + nk \left(\frac{2\pi d}{\lambda} \right) \left[\left(\frac{1 + \sqrt{R_1}}{1 - \sqrt{R_1}} \right) - n_s \right]$$

where n_s = substrate refractive index, n , k = refractive index, extinction coefficient for the thin film, and λ = wavelength.

Similarly, we have for T_1

$$n + \frac{n_s}{n} = (1 + n_s) \left(\sqrt{\frac{T_0}{T_1}} - k \frac{2\pi d}{\lambda} \right)$$

where $T_0 = 4n_s/(1 + n_s)^2$ is the transmittance of the bare.

Given the fringe order, which can be readily determined in this dispersion-free region, and making the substitution

$$\frac{2\pi d}{\lambda} = \frac{(2m + 1)\pi}{2n} \quad m = \text{fringe order} = 0, 1, 2, 3,$$

the equations can be solved simultaneously for n and k ; knowledge of the fringe order then yields d . The effects of substrate back-reflectance were taken into account using the "effective medium" technique utilized by Goodman (11). The value for d , the film thickness, can be independently confirmed from mechanical step height measurements. Once d has been determined, the dispersion relation for n can be determined for the low and moderate absorption regimes from the wavelengths at which successive extrema occur in the transmittance curve. If $T_{\max}$, $T_{\min}$ denote transmittance maxima and minima, then

$$\text{For } T_{\max}: \quad n = \frac{\lambda}{2d} \{1 + m\}$$

$$T_{\min}: \quad n = \frac{1}{d} \left\{ \frac{\lambda}{4} + \frac{\lambda}{2} \right\}$$

where, as before, m is the fringe order. For relatively dispersion-free regions, these values will concur; however, in regions of strong dispersion, they will diverge and an average can be used.

Alternatively the technique of Goodman (11) can be used to evaluate n and d in the long wavelength regime; however, because of the assumptions of transparency and nondispersion, it is not applicable to the moderate absorption regime.

Given d and the dispersion relation for n in the low and medium absorptance regimes, α can be calculated from just the transmittance curve. To facilitate extraction of α from T , a suitable averaging of the transmittance curve envelope was used in conjunction with Connel's formula (10)

$$T = \{(1 - R_1)(1 - R_2)(1 - R_3)e^{-\alpha d}\} / \{1 - R_2R_3 + (2R_1R_2R_3 - R_1R_2 - R_1R_3)e^{-2\alpha d}\}$$

where R_1 , R_2 , R_3 are the reflectances of the air-film, film substrate, and substrate-air interfaces, respectively.

This formula is valid when the summation of the various interference components is incoherent; this is equivalent to defining an "average" transmittance T_{avg}

$$T_{\text{avg}}(E) = \frac{1}{\Delta E} \int_{E-\Delta E/2}^{E+\Delta E/2} T(E) dE$$

Table I. Processing parameters. Deposition temp. = 665°C; N₂ = 23.6 slm; SiH₄ = 28 sccm

Sample	N ₂ O flow (sccm)
1	18
2	25
3	34
4	43
5	65
6	89

where ΔE covers some energy region centered around E covering at least several fringe orders (this scheme is only appropriate for thicker films where the density of fringes is high). This integration can be performed graphically by tracing the envelope of the interference fringes, and, since the correction for substrate back-reflectance is approximately constant, taking some average of this amplitude. Normally this average value will not be 50% due to the asymmetrical nature of the interference patterns. In general, the averaging factor is a weak function of both n and k ; for larger values of refractive index, the deviation from 50% will be greater.

For the purpose of this investigation, a semi-empirical approach was adopted. The low absorption values for n , d , and k obtained from Abeles' equations were substituted into the Connel formula. From this value, a value for the envelope averaging was derived. The variation of the averaging factor due to dispersion were sufficiently small and the envelope amplitude sufficiently small in the high dispersion regions to allow a constant averaging factor to be utilized over the spectrum of interest.

For the high absorption regime, the fringes are no longer present and simpler formulas can be used

$$R = \{[(n-1)^2 + k^2]/[(n+1)^2 + k^2]\}$$

$$T = \{[16n_s(n^2 + k^2)e^{-4\pi kd/\lambda}]/[(n+1)^2 + k^2]\} [(n_s + n)^2 + k^2]$$

where n_s = substrate refractive index, and n, k = film refractive index, extinction coefficient. These equations can be numerically solved with a simple iteration scheme to yield n and α .

There is a small gap between the moderate and high absorption regimes whose reliable extraction of n, k are not possible using the Connel formula and graphical averaging. In this case, one must resort to a solution of the complete equations using algorithms such as those suggested by Tomlin (12). In this study, since the gap was small, of the order of 0.2 eV, such calculations were not deemed necessary.

Results

The film thickness as determined by α -step measurements consistently exceeded those predicted by the optical equations, but the discrepancy was on the order of 2%, and is attributable, in part, to undercutting of the quartz substrate by the etchant.

Figure 1 displays the spectral dependence of α for the as-deposited specimens with relative oxygen content as a parameter. As expected, there is an overall blue shift of α for the higher oxygen content films. Sample 5 exhibited an unexplained, anomalously high absorption for photon energies below 2 eV, although for higher energies, the absorption was in accordance with the overall trend. Values for α less than $2-3 \times 10^2 \text{ cm}^{-1}$ are below the confidence threshold. The shift toward higher energies is essentially a pure translation, with no gross alteration of overall structure. The curves are characterized by piecewise exponential energy dependence, although they appear to approach a weaker, perhaps power law dependence at higher energies.

The absorption coefficient of the films subsequent to annealing are plotted in Fig. 2. There is decreased absorption at higher energies, but a noticeable increase at moderate energies. The annealed curves approach a single exponential dependence upon energy with a reduced slope in the high high energy region as compared to the as-deposited curves. The curves for sample 4 are shown in Fig. 3.

The refractive index for as-deposited and annealed films evaluated in the relatively dispersion-free low absorption regime is displayed in Fig. 4 as a function of nitrous oxide flow rate. The higher oxygen content

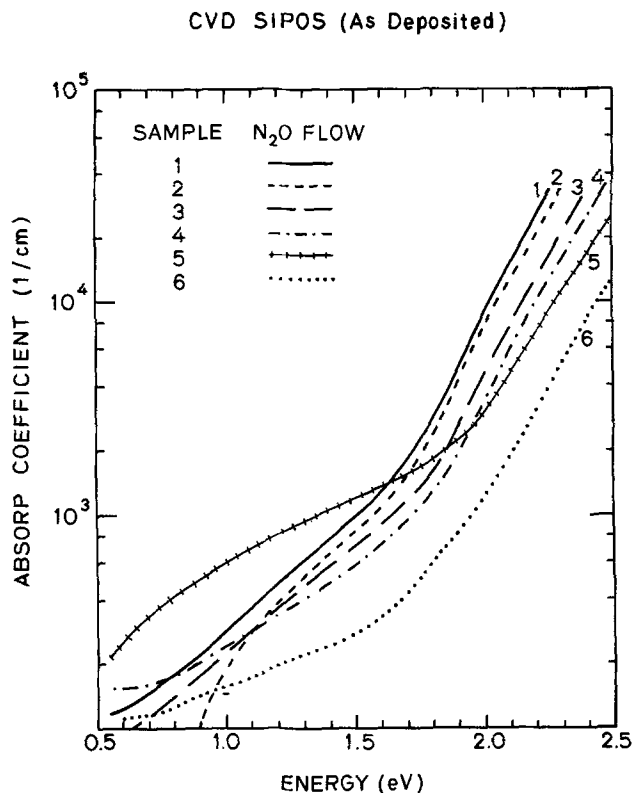


Fig. 1. Optical absorption vs. photon energy for as-deposited films; the parameter is nitrous oxide flow rate used during film deposition.

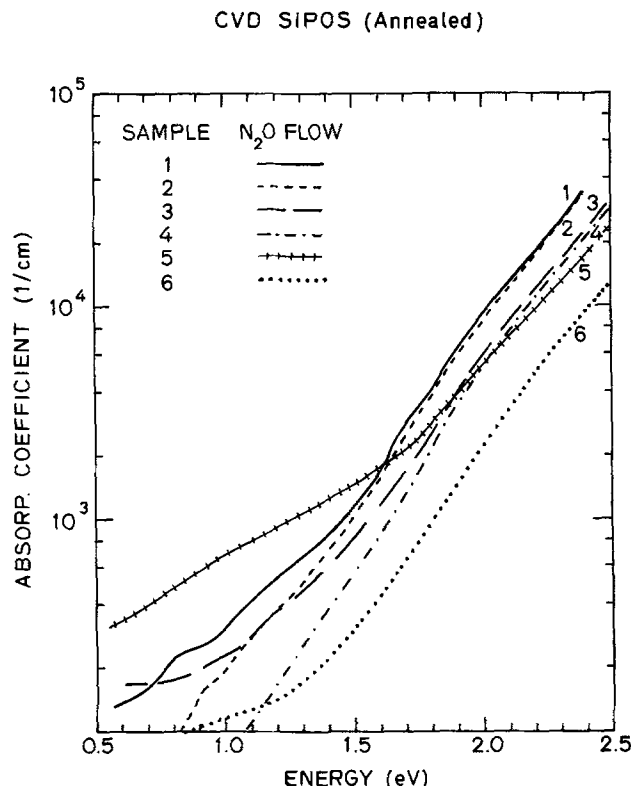


Fig. 2. Optical absorption vs. photon energy for the films subsequent to a 1000°C, 1 hr N_2 anneal; parameter is nitrous oxide flow rate used during film deposition.

films displayed a lower refractive index; annealing the films caused an increase in refractive index for all the samples.

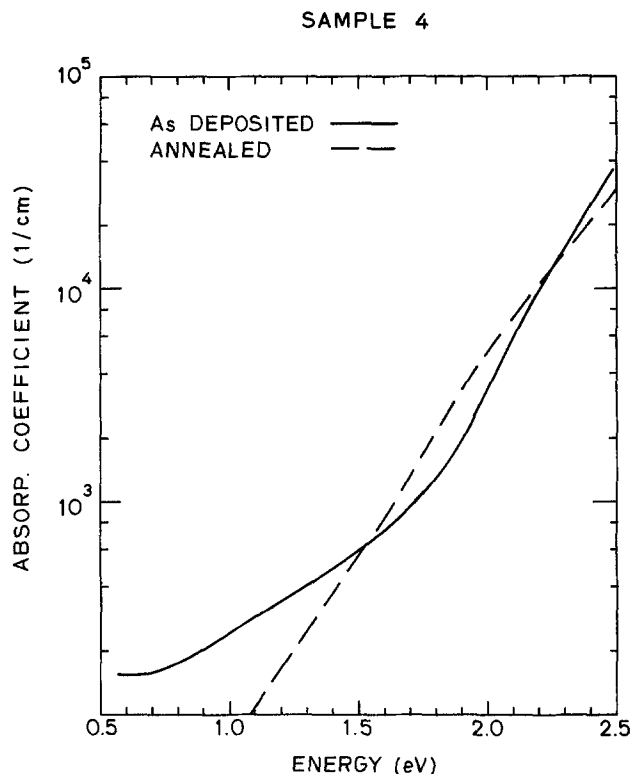


Fig. 3. Optical absorption vs. photon energy for sample 4, comparing as-deposited and postanneal characteristics.

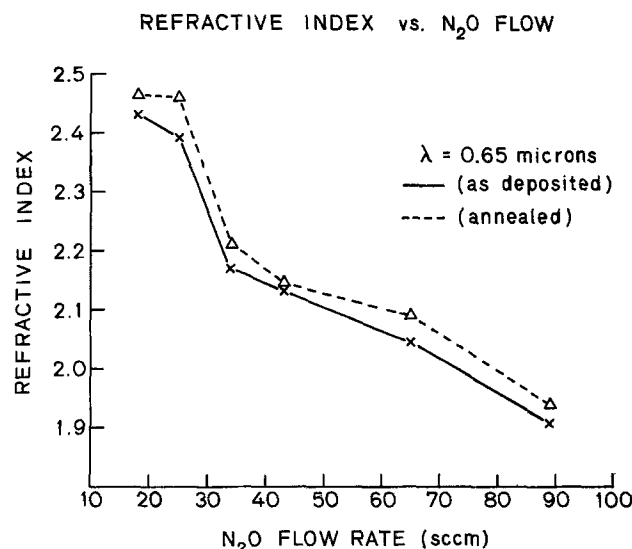


Fig. 4. Refractive index at $\lambda = 0.65\mu$ vs. nitrous oxide flow rate

Discussion

SIPOS films prepared at 650°C are amorphous; TEM examination indicates no structural features larger than $10\text{\AA}$ (7). Since the properties of these films are a smooth function of their oxygen content, the silicon and oxygen atoms appear to be interspersed in an atomically homogeneous distribution. For the relatively high deposition rates associated with atmospheric pressure CVD films, the distribution of oxygen atoms appears to be determined primarily by statistics (14). Consequently the most favored configuration in a tetrahedral structure will vary from $\text{Si}-(\text{Si}_4)$ to $\text{Si}-(\text{Si}_3\text{O})$ to $\text{Si}-(\text{Si}_2\text{O}_2)$ to $\text{Si}-(\text{SiO}_3)$ to $\text{Si}-(\text{O}_4)$ as x is varied from 0 to 2.

High temperature annealing converts these amorphous films into a multiphase network. The presence of islands of $\alpha\text{-Si}$ and SiO_x ($x < 2$) which are gradually

annealed into crystalline $\alpha\text{-Si}$ and SiO_2 , embedded in a connective matrix has been postulated (7, 8). This connective matrix is probably $\alpha\text{-Si}$ for films with low oxygen content, gradually changing to SiO_x , where x increases with increasing oxygen concentration, but remains below the stoichiometric value of 2. Sheet resistance studies indicate that the films used in this study are predominantly of the former type.

For the amorphous, as-deposited films, if we assume that optical properties are dominated by short range order, as in Philipp (13), then the absorption in this low energy range should be dominated by the density of Si-Si bands and by the nature of their local environment. For higher oxygen concentrations, the density of Si-Si bonds decreases, and the local environment of these Si-Si bonds is likely to be dominated by Si-O bonds. The absorption coefficient in these SIPOS films does display a slight blue shift corresponding to a shift in Si-Si absorption to higher energies; the marked reduction in absorption can be attributed to the reduced density of such bonds.

Annealing these films increases the probability of clustering of $\text{Si}-(\text{Si}_4)$ tetrahedra in the form of microcrystallites. If short-range order dominates optical behavior, then these microcrystals should display absorption characteristics similar to that of bulk amorphous silicon. Since the local environment of the Si-Si bonds is different in these microcrystals, the absorption is expected to move to lower energies, while keeping the total contribution to the oscillator strength relatively constant. The increased absorption at moderate energies at the expense of higher energy absorption observed for these films is consistent with such a model.

It is also observed that for samples 4 and 6, with higher oxygen concentration, annealing decreased absorption in the 1.0-1.5 eV range. For this range of energies, absorption is probably attributable to defect states, potential fluctuations, etc. in the material. Annealing usually decreases the concentration of such defects and would be expected to lower the contribution from this mechanism. However, the lower oxygen content films did not display a significant change in characteristics in this energy range suggesting a possible dependence of defect density and type on oxygen concentration.

For these samples, it did not prove feasible to extract an "optical gap" from a $\sqrt{\alpha h\nu}$ vs. $h\nu$ plot of absorption coefficient; a linear relationship can be expected if one assumes a momentum matrix element insensitive to energy and a density of states that has a parabolic dependence on energy. While such conditions may hold for higher energies, they do not appear to do so for the range of energies covered by this study.

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Evaluation of Pure Novolak Cresol-Formaldehyde Resins for Deep U.V. Lithography

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ABSTRACT

A series of pure, isomeric cresol-formaldehyde novolak resins have been synthesized and evaluated with respect to their utility as matrix resins for deep u.v. resist formulations. One of the cresols, the p-isomer, provides a resin which has far greater optical transmission at 254 nm than the commercial cresylic acid novolaks used to formulate the classical positive photoresists. Synthetic procedures were developed which allow reproducible preparation of the p-cresol novolak over a wide range of molecular weights including that region which displays base dissolution kinetics that are compatible with lithographic processing.

The need for higher density circuitry in microelectronic devices has promoted interest in a variety of lithographic techniques which are designed to provide higher resolution than the optical exposure tools presently in use throughout the industry. The current tools accomplish resist exposure utilizing radiation from a mercury source in the 404 nm region. A number of theoretical and experimental studies have shown that utilizing the 254 nm rather than the 404 nm mercury emission results in approximately a twofold increase in resolution, other factors remaining constant (1-4). Lithography based on radiation at 254 nm has been termed deep u.v. lithography (1).

Several manufacturers have made or plan to make available sophisticated aligners and exposure tools designed to provide deep u.v. radiation at the resist surface. In order to utilize this radiation and to realize the potential resolution enhancement, new mask systems and new resists must be developed. Supersil quartz masks with thick chromium or iron oxide contrast elements are presently available. However, at this time, there is no resist available which functions satisfactorily in the deep u.v.

Poly(methyl methacrylate) (PMMA) was reported to be sensitive to deep u.v. radiation (5) and very high resolution images have been contact printed in this resist using 254 nm radiation (1, 2). However, the dose required to achieve good image quality and useful processing is very high. Also, the flux at 254 nm provided by exposure sources based on mercury emission is so low that exposure times using PMMA are excessive.

The classical photoresists are also unsatisfactory in the deep u.v. These resists consist of a radiation insensitive novolak-type matrix resin in which is dissolved a radiation sensitive organic compound. This type of formulation is the basis of many of the commercial positive resists. The photoactive compound (PAC) is a substituted diazo naphthoquinone and the matrix is a cresylic acid-formaldehyde resin (6, 7). The PAC acts as a dissolution rate inhibitor for the matrix resin in the unexposed imaging layer. In the exposed regions, the PAC undergoes a radiation-induced structural

transformation which greatly alters its efficiency as a dissolution rate inhibitor for the novolak resin (8). Consequently, the exposed regions are rendered more soluble than the unexposed regions and the difference in solubility rates is utilized to generate the lithographic patterns.

Two important factors contribute toward limiting the utility of such resists in the deep u.v. First, the PAC absorption at 254 nm, though intense, does not bleach as it does at 404 nm. The photoproducts absorb at 254 nm. Secondly, the matrix resin which is essentially transparent at 404 nm has a strong absorption at 254 nm. The combined absorption of the PAC and the resin renders films more than 1 μ m thick virtually opaque at 254 nm. No radiation reaches the PAC at the resist substrate interface. Attempts to photodecompose the PAC by extending the exposure times serve only to overexpose the upper levels of the resist and result in degradation of the profiles.

During the last several years, there has been a concerted effort by researchers throughout the semiconductor industry to develop a usable deep u.v. resist system. In all reports available to date, these efforts have centered around systems similar to PMMA. In particular, poly(methyl isopropenyl ketone) (PMIPK) doped with certain sensitizers has demonstrated a usable sensitivity (9). However, PMMA and its derivatives, and all aliphatic polymers, including PMIPK, are unsuitable masks for RIE or plasma processing. These materials are removed under plasma condition at rates several times that of conventional photoresist (10).

We have attempted to design a deep u.v. resist system which is comparable in both speed and etch resistance to the commercial photoresists. The etch resistance of these materials is a reflection of the aromatic structure of the matrix resin while the radiation sensitivity is dependent upon the structure of the sensitizer. However, commercial photoresist formulations are very complex mixtures of novolak resins, sensitizers, additives, and solvents (11). Therefore, it was our contention that a single high purity novolak resin with a controlled molecular weight, when combined with a compatible sensitizer, would more readily permit the optimization potential for control of the lithographic process (12).

Key words: polymers, ultraviolet, integrated circuits.