Research On

THE PROCESSING OF ELECTRONIC MATERIALS

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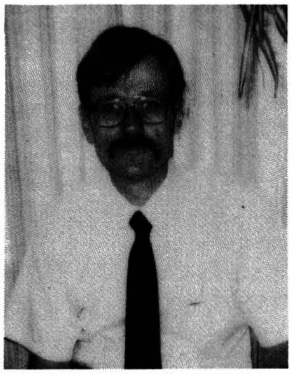
FOR SEVERAL YEARS, the chemical engineering department at Clarkson has been actively involved in the area of materials processing. One of our major areas is the processing of electronic materials: the production of high purity bulk crystals, the fabrication of integrated circuits, and the manufacturing of printed circuit boards. Several of the faculty have worked in the electronics industry, either during the summer or on sabbatical leave, or as consultants. We have also benefitted from a graduate "co-op" program with industry in which graduate students spend six to nine months doing their thesis research at an industrial site. In this way, they can take full advantage of a wide variety of modern equipment and qualified technicians that is often not available at a university.



Suryadevara V. Babu has been a professor of chemical engineering at Clarkson since 1981. Prior to that he was on the faculty at Indian Institute of Technology, Kanpur. He spent 1969-70 at the Niels Bohr Institute in Copenhagen, Denmark, and at the International Center for Theoretical Physics, Trieste, Italy, and was a post-doctoral fellow at New York University from 1970 to 1972. His interest in electronics manufacturing is of recent vintage, and grew out of several summers spent with IBM. He has taught an undergraduate course, "Packaging for Electronics," and a graduate course, "Integrated and Printed Circuit Fabrication," several times at Clarkson. **(L)**

Peter Sukanek received his PhD from the University of Massachusetts. After four years with the Air Force Rocket Propulsion Laboratory, he joined Clarkson's chemical engineering department in 1976. He spent the summer of 1982 with IBM in Essex Junction, Vermont. Together with Bill Wilcox, he has been teaching a short course on integrated circuit fabrication. He is currently on a sabbatical with Phillips Research Laboratory in Netherlands. **(R)**

In this article, we will discuss some, but not all, of the ongoing research. Other areas of research that will not be described include Bill Wilcox's work on crystal growth, both on the ground and in reduced gravity environments, Don Rasmussen's work on nucleation and chemical vapor deposition of refractory materials for integrated circuit metallization, and Sandra Harris's efforts to apply adaptive control techniques to the electroless plating of printed circuit boards.

The production of integrated circuits or printed circuit boards involves the creation of successive layers of different patterns in materials. These patterns might be regions of semiconductor (such as silicon) doped with different materials (such as boron or phosphorous) to form transistors, regions of conductors (such as aluminum or copper) to form electrical connections, and regions of insulating material (such as silicon dioxide or an organic polymer) to isolate the conductor lines. Much of our research is involved with the formation of these patterned regions. Below, we discuss our efforts in the areas of resist materials, etching and laser processing.

RESIST MATERIALS

The most common method of creating these patterns is to coat the substrate with a radiation sensitive organic material and then to illuminate the coating with radiation of the appropriate wavelength through a mask, as illustrated in Figure 1. If the illuminated material is more soluble in a developer, it is referred to as positive type, and if it is less soluble, as a negative type. The pattern is transferred to the underlying layer in an etching step. Since the radiation sensitive material is (ideally) unaffected by the etchant, it is called a "resist."

In the production of integrated circuits, it is often essential that the resist coating be both thin (on the order of 1 μm) and uniform (on the order of ± 100 Å or less). Otherwise, uniform patterns cannot be obtained across the surface of the substrate. These films are created by spin coating. A small amount of resist solution is deposited onto the surface of the wafer, which is then rotated at speeds of several thousand rpm's. The coating thins by a combination of flow across the surface of the substrate and by evaporation of the solvent.

We have developed a mathematical model for the coating to understand the parameters which control the film thickness and to predict the conditions when nonuniform films might be expected. The model assumes a two component material, containing both volatile and non-volatile species, which accounts for the mass flux from the surface from evaporation of the solvent [1]. The model correctly predicts the variation of thickness with spin speed. In addition, the model is in qualitative agreement with available data on the effects of initial viscosity and solvent volatility. Uniform films can always be obtained except when the surface mass transfer becomes turbulent or for certain spin speeds with non-Newtonian fluids.

There are still a number of important items missing from the model. In particular, we have neglected diffusion of the solvent within the resist film and the dependence of the diffusivity on the solvent concentration. By including these factors, we hope to model the conditions under which small irregularities in resist height, called "orangepeel," occur. In addition, residual solvent also has an effect on subsequent resist processing. Another factor to be added to the model is the effect of substrate features, such as steps, on the film uniformity.

Dry film negative photoresists are commonly used in the manufacture of additively plated printed circuit boards. The resist is crosslinked on exposure to UV-radiation either by photo-polymerization or by nitrene insertion into the carbon-carbon double bonds of the polymer [2]. Crosslinked regions of the resist are insoluble.

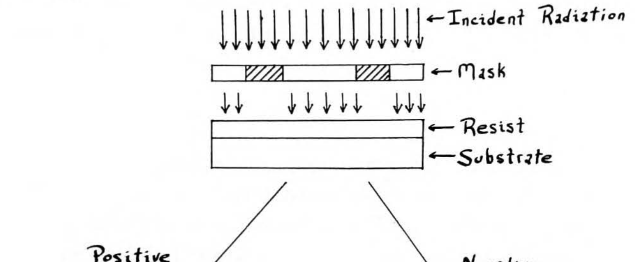


FIGURE 1. Positive resists are less soluble after exposure; negative resists are more soluble.

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Maintaining adequate adhesion to the substrate, as well as preserving the line profiles in such resists, demands crosslink uniformity in the exposed regions and minimal solvent-induced swelling throughout the resist film on development. Incident radiation is strongly absorbed in the top layers of the thick resist film, leading to a lower degree of crosslinking at the resist-substrate interface. Solvent penetration along this interface can cause undercutting and delamination of the resist. Increasing the incident energy dosage, on the other hand, will produce a brittle resist layer at the top. Optimization of the exposure and development processes has been investigated by measuring the crosslink gradient using successive solvent extractions. The exposed resist-substrate adhesion correlates inversely with the degree of crosslinking at the interface [3]. A mathematical analysis of the polymerization kinetics has been carried out which showed that, in a first approximation, the contrast of the resist is inversely proportional to its optical density [4].

In the manufacture of VLSI devices, positive photoresists are widely used. Exposure to radiation converts a photoactive compound (PAC) to a carboxylic acid [5]. The exposed regions, containing the resin and the acid, dissolve faster than the unexposed regions in aqueous basic solvents.

As in the case of the negative resists, the radiation intensity is not uniform in the resist film due to absorption. A pair of coupled nonlinear partial differential equations, one for the UV-intensity in the film and the other for the concentration of the PAC, describe the kinetics [6]. A rigorous and complete mathematical description is complicated because of interference between the incident beam and its multiple reflections from the resist-substrate and resist-air interfaces causing a standing wave pattern [7]. However, there are instances of practical importance where the substrate is strongly absorbing. The exact solution has been obtained for such situations, and has been used to determine the resist contrast in a closed form [8].

The solution has been extended to the case of contrast enhanced lithography (CEL) [9]. In this method, a thin dye or polysiloxane film on the resist improves its contrast (*i.e.*, gives steeper side wall angles). Finally, the model has also been applied to the image

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reversal process [10], where an additive to a positive acting resist converts it to a negative one without any swelling-induced distortions.

Once images are formed in the resist, the pattern is transferred to the underlying layer in an etching step. In many dry etching operations, where the wafers are exposed to a gas plasma, surface reactions and ion bombardment cause the temperature to rise. If the temperature is too high, the resist "reflows." Line widths and angles change, changing the shape of the etched region. In some gas environments, the combination of increased surface temperature, resist surface reactions, and solvent evaporation cause the resist to "reticulate." Under a microscope, the resist appears to have changed from a smooth surface to one which is severely wrinkled. In many cases the resist becomes quite difficult to remove, even with very aggressive solvents.

We have begun to investigate the cause of these phenomena [11]. They are related to the chemical make-up of the resist materials, the amount of solvent still remaining in the resist, and the surface tension induced flows in the resist images during heating and etching. At sufficiently high temperatures, chemical reactions in positive resist can cause crosslinking. In many cases, before these crosslinking reactions make the images immobile, the residual solvent lowers the glass transition temperature sufficiently to cause image deformation. Chemical modifications of the resist surface during an etch of the underlying film changes the surface properties and can alter the extent of the modification.

One way to avoid image deformation is to treat the resist before it is subjected to high temperature. One recently popular method is to use ultraviolet light at a wavelength where the resist material strongly absorbs. In this way, the effect of the radiation is localized to the resist-air interface. We have been examining the relationship between processing conditions and image size and shape, trying to optimize the treatment for different applications [11]

ETCHING

To replicate the resist pattern in the underlying layer, an etching step is used. Originally, a liquid solvent was employed. For example, if silicon dioxide were to be patterned, the resist coated wafers were immersed in a hydrofluoric acid bath. The HF dissolves the oxide, but leaves the resist and the silicon untouched. As discussed below, such "wet" etching methods are being replaced by dry or plasma etching. However, the method is still in widespread use.

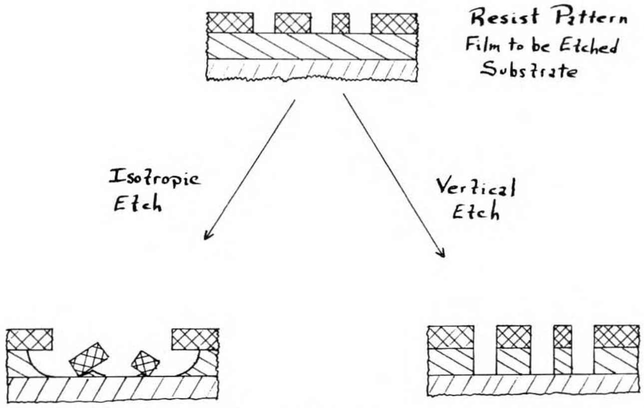

FIGURE 2. Wet etching is usually isotropic, and leads to problems patterning small dimensions. Plasma etching is often directional.

We have studied the etching of silicon dioxide by buffered HF solutions to determine the effect of processing conditions on the etch rate. In some cases it is possible that certain images, with sizes from 3 to 10 μm, will etch at a much slower rate than those of other sizes. We have shown that this is due to air bubbles trapped in the cavities. A thermodynamic analysis of the stability of the bubbles as a function of such variables as surface tension and resist sidewall angle correctly predicts whether or not the images will etch [12].

One of the reasons wet etching has declined in use is that the etching is usually isotropic, proceeding at the same rate in both the lateral and vertical directions. As illustrated in Figure 2, this limits the density of images which can be reproduced on the surface. In many instances, directional etching can be achieved by etching in a reactive gas environment formed in a glow discharge. This method is called plasma etching or, when there is ion bombardment of the material to be etched, reactive ion etching. The radicals and/or ions in the plasma discharge react with the film to form volatile species. The discharge consists of mostly undissociated feed gas molecules, very energetic electrons (with temperatures exceeding 20,000K), neutral radicals, and negative and positive ions. The plasma is not in thermal equilibrium, as the temperature of the heavier species is only about 500K. Nevertheless, the processes occurring in a plasma reactor are akin to those in conventional gas-solid reactions: generation of reactive species in the gas phase, diffusion of these species, adsorption on the solid surface, surface reaction, product desorption, and product diffusion. Different steps control the etch rate in different etching systems.

The discharge is sustained by an RF power supply.

The presence of associated electric fields significantly complicates the chemical kinetic analysis of such systems. Modeling the electron, ion and radical transport and the coupled chemical kinetics under these conditions is an active area of current research at Clarkson. A program available from the Joint Institute for Laboratory Astrophysics in Boulder [13] has been modified and extended to calculate the electron energy distribution functions and the associated rate constants for a large number of simultaneous reactions occuring in the plasma discharge. Polymer and silicon etch rates in $CF_4 + O_2$ discharges have been modeled under steady state conditions [14].

We have also been studying the reactive ion etching of silicon dioxide, and metals and metallic compounds. Using a simple mechanism for oxide etching, we have developed a model for the etch rate which does an excellent job in correlating data from a number of different reactor geometries [15]. The DC bias of the oxide surface appears to be one of the most important factors in determining the oxide etch rate. For metal etching we are using a technique called reactive ion beam etching.

Plasma processing was first used to remove organic polymeric materials. In the manufacture of multi-level printed circuit boards (PCB's), plated through-holes extending from the top to the bottom of the board facilitate buried signal and power plane interconnections. Under high speed drilling conditions, the temperature of the dielectric organic material between the conductors exceeds the glass transition temperature, and the conductors are covered by a very thin layer of the dielectric. This smear consists of the organic and fine pieces of the glass reinforcing material present in the laminate. Desmearing of the conductors before plating the through-holes can be achieved in $CF_4 + O_2$ plasma disharges [16].

Considerable effort has been devoted to elucidate the complex chemistry of the etching of organic polymers in $CF_4 + O_2$ plasma discharges. At low (<30%) CF_4 concentrations in the feed gas, the steady state etch rate of organic polymers is significantly enhanced over that in pure oxygen. An increase in the gas phase concentration of atomic oxygen and the faster hydrogen abstraction by flourine atoms are primarily responsible for this increase. At higher CF_4 concentrations, however, inert fluorocarbon moeities form on the polymer surface and inhibit the etching process. We have studied the role of these competing mechanisms in determining the etch rate [17]. It has also been discovered that the etch rate of organics, as measured by laser interferometry, increases "momentarily" by several orders of magnitude before returning to the normal steady state value when the feed gas composition is switched from one that is rich in CF_4 to pure O_2 [18]. Such a transient response is not completely understood yet. Emission spectroscopy and laser induced fluorescence are being used to measure the concentrations of the short-lived reactive species in order to understand more about etch mechanisms.

EXCIMER LASER PROCESSING

The use of lasers in electronics manufacturing is widespread and is gathering momentum. Several innovative applications have been proposed. These include direct writing, maskless dry lithography, enhanced plating, metal deposition, repair of open conductors, drilling, annealing ion implanted damage, polysilicon recrystallization, oxide growth, etc. At Clarkson an excimer laser operating at 194 and 245 nm has been employed for drilling polyimide, for copper deposition, and for establishing the feasibility of sub-micron etching of polysilicon with NF_3.

Polyimide is used as innerlevel dielectric in multichip VLSI packages [19]. Electrical contact between signal planes can be established by drilling vias in polyimide and plating them with copper. Intense (up to 10 J/cm^2 fluence) pulses have been employed in this study and drill rates of about a micron per pulse have been attained. Both a photochemical and a thermal mechanism contribute to the polymer ablation [20]. Plating of copper films has been achieved in preliminary experiments in which spin coated films of copper formate are exposed to the excimer radiation [21]. Polysilicon is etched by F-atoms obtained by the laser induced dissociation of NF_3. The NF_3 molecules are adsorbed on the polysilicon surface at sites generated by the incident laser pulse. The adsorbed molecules dissociate on the surface, and the F-atoms generated are highly reactive and etch the polysilicon locally. If lateral diffusion of the F-atoms is indeed negligible then direct writing of sub-micron lines on polysilicon should be feasible [22].

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REFERENCES

1. Sukanek, P. C., "Spin Coating," *J Imaging Tech*, **11**, 184, (1985)
2. L.F. Thompson, C. C. Willson and M. J. Bowden, editors, "Introduction to Microlithography," ACS Symposium Series 219, Washington DC, (1983)

3. R.L. Geary, S. V. Babu and J. Stephanie, in the Proceedings of the Symposium on Surface and Colloid Science in Computer Technology, K. L. Mittal, Editor, Potsdam, 1985 (in Press)
4. S.V. Babu and V. Srinivasan, *IEEE Trans Electron Dev* **ED-32**, 1896 (1985) and *J.Imaging Tech.* **11**, 168 (1985)
5. J. Pacansky and J. R. Lyerla, *IBM J Res and Dev* **23**, 42, (1979)
6. F. H. Dill, W. P. Hornberger, P. S. Hauge and J. M. Shaw, *IEEE Trans Electron Dev* **ED-22**, 445 (1975)
7. F. H. Dill, A. R. Neureuther, J. A. Tuttle and E. J. Walker, ibid, **ED-22**, 456 (1975)
8. S.V. Babu and E. Barouch, *IEEE Electron Dev Lett* **EDL-7**, 252 (1986)
9. S. V. Babu and E. Barouch and V. Srinivasan, Submitted to *IEEE Trans Electron Dev*
10. S. V. Babu, *IEEE Electron Dev Lett* **EDL-7**, 250 (1986)
11. Sukanek, P. C., "Physical and Chemical Modifications of Photoresist," in P. Stroeve (ed), Chemical and Physical Processing of Integrated Circuits, ACS Symposium Series No. 290, **95**, 1985
12. McAndrews, K. and P. C. Sukanek, "Nonuniform Wet Etching of Silicon Dioxide," submitted for publication.
13. W. L. Morgan, JILA Information center report No. 19, Boulder, Colorado, 1979
14. V. Srinivasan, M. S. Sivasubramanian, and S. V. Babu, Proceedings of the 7th International Plasma Chemistry Symposium, p1405, C. J. Timmermans (Editor), Eindhoven, 1985; and T. Daubenspeck and S. V. Babu (to be published)
15. Sullivan, G. and P. C. Sukanek, "A Simple Model for Reactive Ion Etching of Silicon Dioxide," submitted for publication
16. R. D. Rust, R. J. Rhodes, and A. A. Parker, *Solid State Tech* **27**(4), 270 (1984)
17. S. V. Babu, L. Tiemann, and R. E. Partch, Proceedings of the 7th International Plasma Chemistry Symposium, p1025, C. J. Timmermans (Editor), Eindhoven, 1985
18. J. F. Rembetski, M.S. Thesis, Clarkson University (1985), and J. F. Rembetski, W. E. Mlynko, J. G. Hoffarth, and S. V. Babu, ibid, p1100
19. R. J. Jensen, J. P. Cummings, and H. Vora, *IEEE Trans Comp Hybrids and Manuf Tech* **CHMT-7**, 384 (1984)
20. V. Srinivasan, M. Smrtic, and S. V. Babu, *J App Phys* **59**, 3861 (1986)
21. M. Ritz and S. V. Babu, (unpublished)
22. M. Armacost, M.S. Thesis, Clarkson University (1986) □

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