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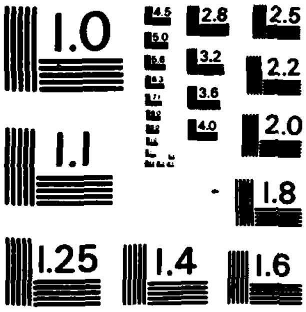

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LASER PHOTODEPOSITION AND PHOTOETCHING STUDY

Progress Report

to

Air Force Office of Scientific Research

and

Defense Advanced Research Projects Agency

1 January 1983 - 31 March 1983

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## 1. Introduction

Work during this quarter has developed a new technique for direct-write etching of Al and Al:Si:Cu alloys, and has applied this new process to correction of bridging faults in VLSI signal-processing circuits. Additional work has expanded upon two excimer-laser resist processes to develop fast deep-UV lithographic procedures based on these powerful UV sources. A final series of experiments has extended pulsed UV-laser reactions to area photodeposition of $Al_2O_3$ films.

## 2. Al and Al-Alloy Etching by Laser Passive-to-Active Transition Switching

The Al etching technique is based on a carefully engineered wet electrochemical process in which focused laser radiation is used to switch a passive-to-active transition in the reactivity of phosphoric acid/nitric acid electrolytes. This approach was chosen as a method to minimize the laser-induced temperature excursion of fragile circuit areas, while maintaining a large etch-rate contrast between laser-irradiated areas and background etching of the circuit under immersion in the electrolyte. A contrast of greater than $10^4$ in rates is needed for most practical implementations in VLSI repair. We have found that values greater than $10^7$ can, in fact, be obtained in well balanced solutions using dichromate-ion surfactants, as described in some detail in the enclosed paper. The reaction has also been optimized for the $Al_{0.95}Cu_{0.04}Si_{0.01}$ alloys used in our current circuits.

The new technique has several practical advantages over existing laser-ablative methods with respect to resolution, control, and greatly reduced process temperature. Although the technique requires substrate immersion, the etchant has been optimized to be non-corrosive at ambient temperature. Consequently, it may be widely useful for removing excess Al left by random patterning errors in integrated-circuit fabrication and for cutting links on redundant or custom circuitry. To demonstrate this, we have made laser exposures of integrated-circuit metallization patterns using a cw $Ar^+$ laser combined with a high-magnification optical microscope both to focus the laser beam onto the substrate and to allow in situ viewing of the etching process. Figures 1 and 2 show scanning-electron micrographs of a laser-etched cut in a 200-nm-thick conductor and, for comparison, a conductor disrupted by irradiation in air. Four shuttered, 100-ms laser pulses were used in each case; however, the power level required for chemical etching is ~ 0.12 W, whereas that required for complete ablation in air is ~ 0.4 - 0.5 W. Based on cross calibrations the peak temperature during etching is estimated to be ~ 200°C. Equivalent results were obtained with unsintered and sintered films of both Al and $Al_{.95}Cu_{.04}Si_{.01}$. The improved edge control and spatial resolution associated with chemical etching is significant; a minimum width of ~ 1.5 μm was demonstrated here for 0.2-μm-thick metal films on 1-μm-thick $SiO_2$ on Si wafers. The high spatial resolution possible for such thermally activated reactions, even on good thermal conductors, has been discussed previously.

## 3. Excimer-Laser Resists

Two new excimer-laser resist materials have been developed in order to explore the potential of optimized materials with these powerful deep-UV sources for practical lithography. The first is based on Ag photodoping of $GeSe_x$ alloys similar to those developed by Kawamura et al. and Tai et al. for high contrast lithography by lamp or e-beam exposure. We have developed a similar silver-sensitized $GeSe_2$ alloy and characterized the exposure of this

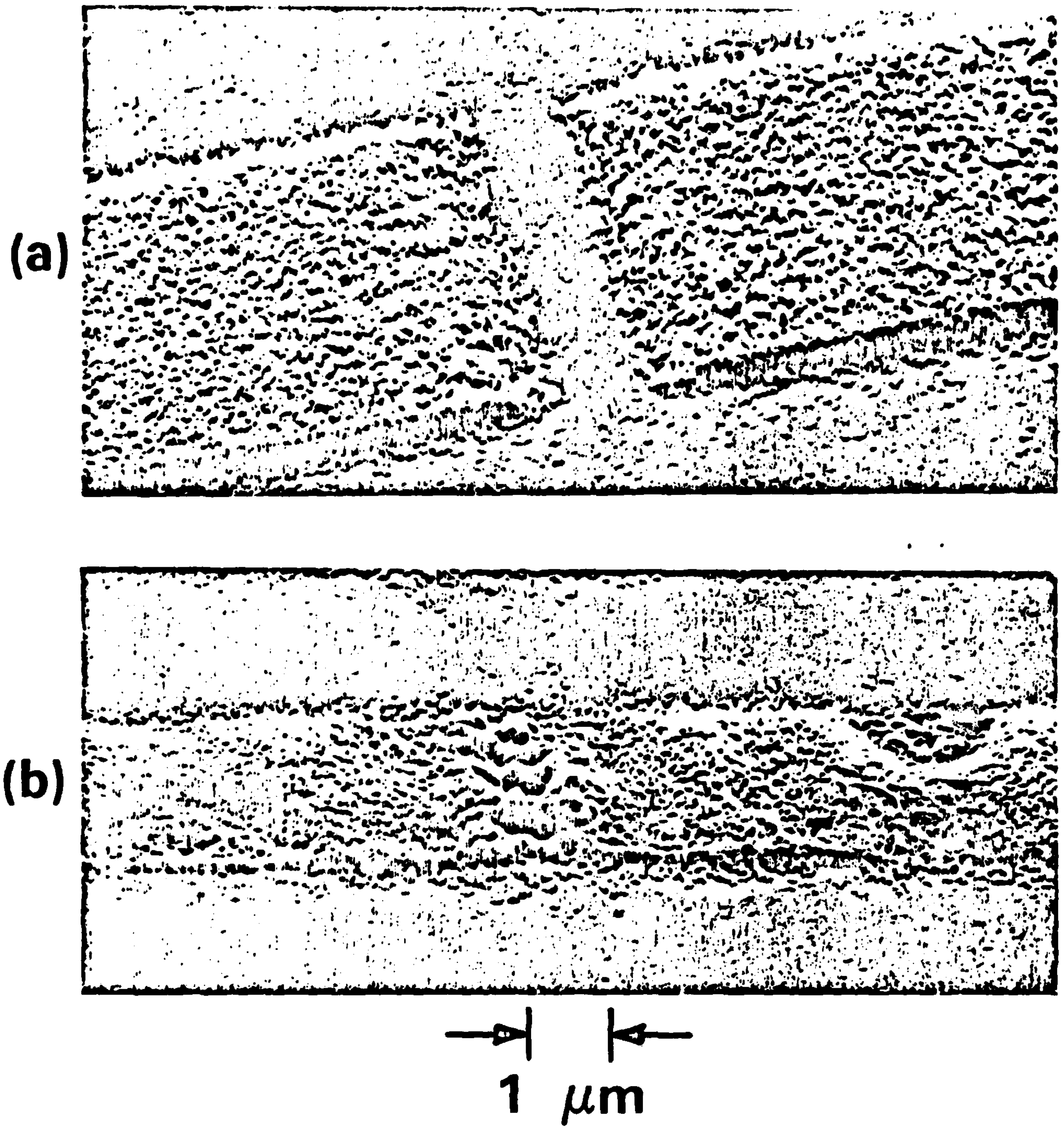

Fig. 1. Comparison of (a) laser etching, and (b), laser ablation of Al metallization. Higher laser powers, creating oxide damage, are needed for complete ablation.

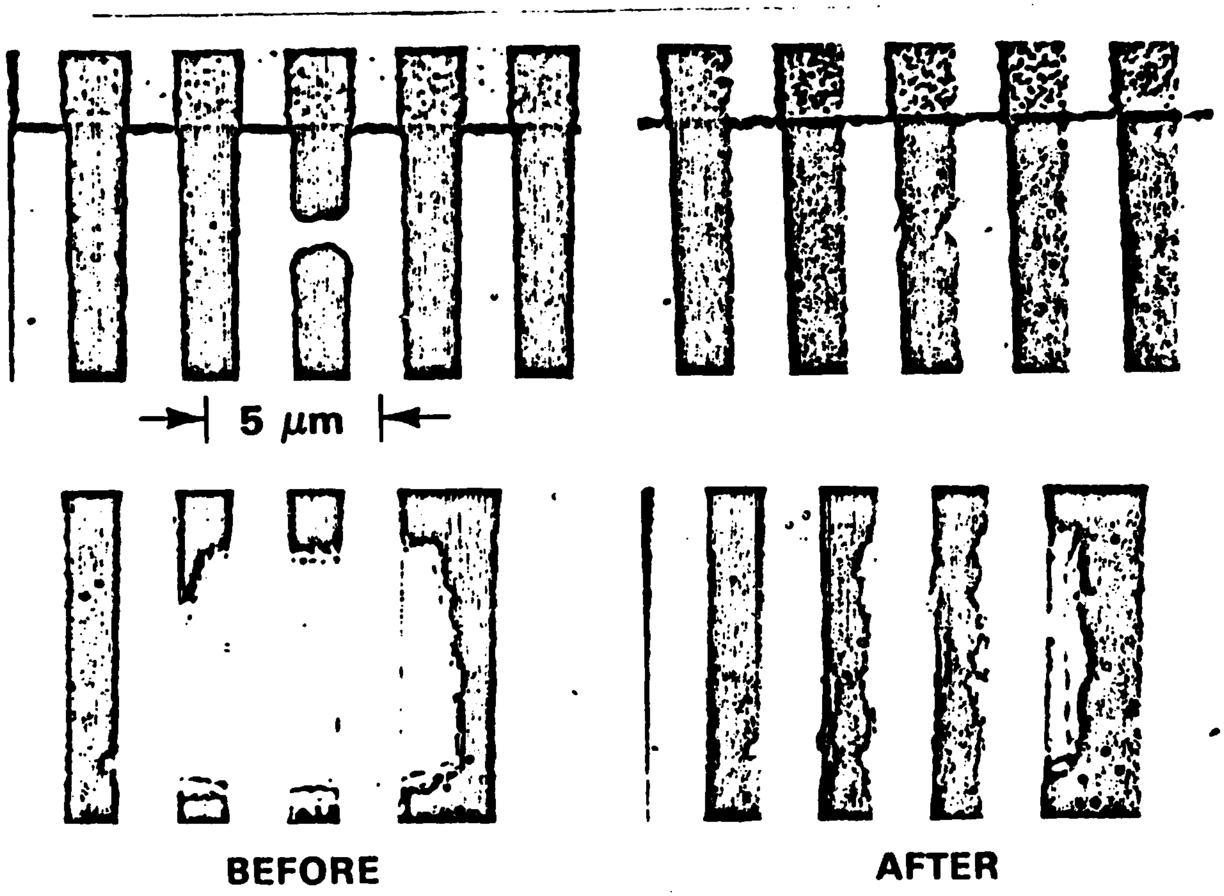

Fig. 2. Laser chemical etching used for correction of metallization bridging faults in a VLSI signal-processing circuit.

material under ArF (193 nm) and KrF (249 nm) irradiation. A exposure threshold of 5 mJ/cm$^2$, the highest sensitivity by far yet found for any deep UV resist, is obtained by taking advantage of the short (10 ns) pulsed output of these excimer laser sources. A scanning electron micrograph of 0.5 µm lines and spaces produced by contact printing is shown in Fig. 3.

The second material examined, nitrocellulose, functions as a photoresist which can also be patterned directly using pulsed excimer laser radiation. This resist exhibits a somewhat higher exposure threshold of 20 mJ/cm$^2$ at a wavelength of 193 nm; however, it is a self-developing resist which can be patterned by ablation without a development step. The resolution, inferred from optical diffraction from an edge, is better than 0.3 µm. A reprint describing early results with this photoresist is enclosed.

## 5. UV Photodeposition of $Al_2O_3$

Low-temperature deposition of insulating films is of interest as a technique for semiconductor processing that can reduce wafer warpage and undesired chemical reactions in Si technology and allow greater processing flexibility. The method has potential applications in III-V semiconductor technology, where processing temperatures must be kept low in order to avoid material dissociation. In recent experiments we have deposited films of $Al_2O_3$, a material of interest as a dielectric for use with InP and GaAs as well as with Si, and evaluated its properties. In addition, the effect of UV irradiation of the surface during deposition has been examined.

A pulsed ArF excimer laser was used to dissociate the reagent gases, trimethyl aluminum, TMA, and $N_2O$. The substrates were heated to temperatures of 200-500°C. Under normal conditions, the laser beam, collimated by a beam reducing telescope to a slit image about 3 x 25 mm, passed about 1 mm

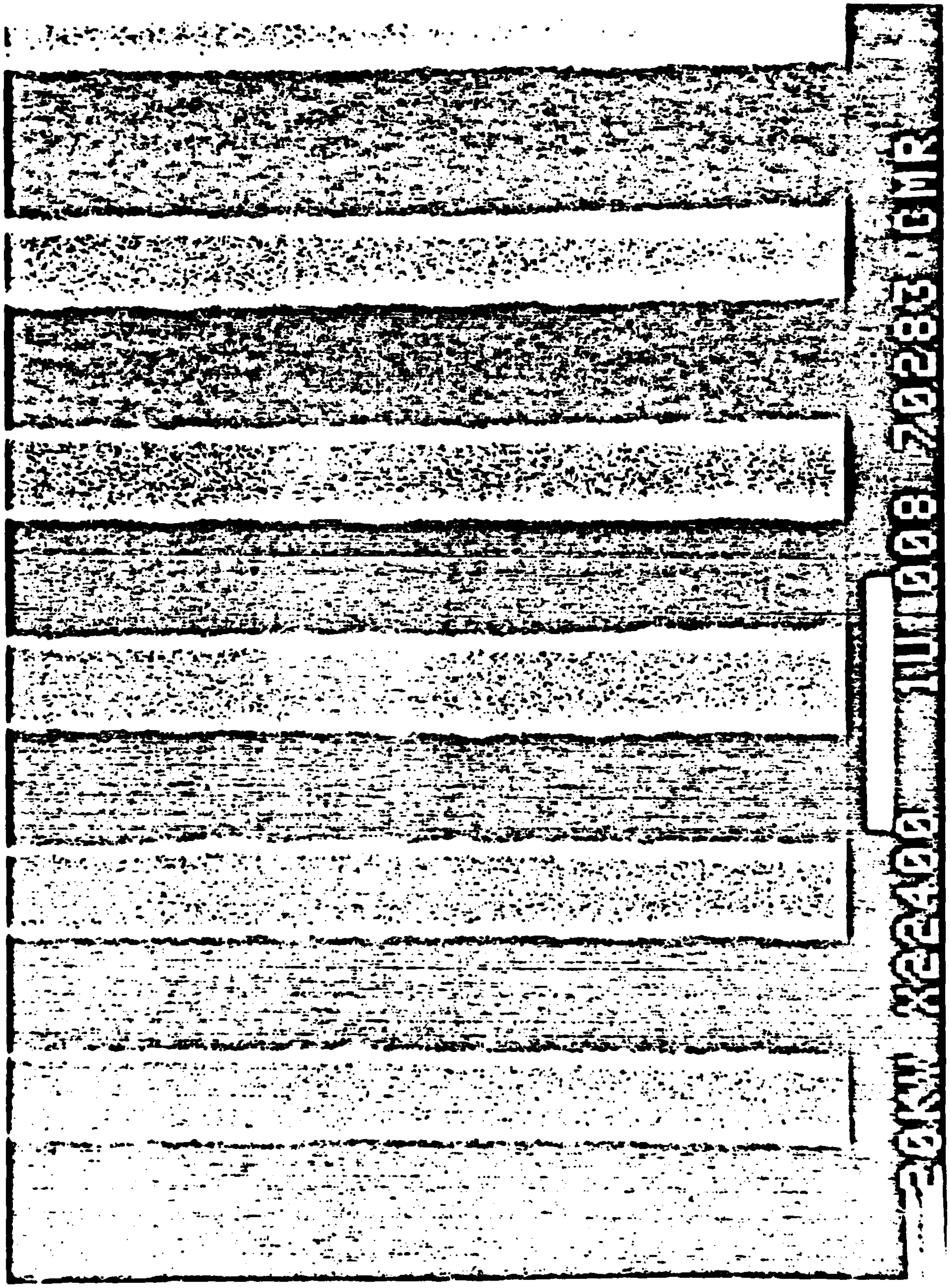

Fig. 3. Scanning electron micrograph of 0.5 μm lines and spaces by excimer-laser exposure of $GeSe_2$ photoresist.

above the substrate. In some experiments, the beam exiting from the deposition chamber was folded back by mirrors and used to irradiate a portion of the substrate.

The deposited films were examined by ellipsometry, Auger electron spectroscopy (AES), and by capacitance-voltage (C-V) measurements made on films contacted by indium dots. The refractive index of the deposited films, which were 100-200 nm thick, ranged from 1.5-1.7; single crystal $Al_2O_3$ has an index of 1.76, and values of 1.64 are typical of films deposited by other techniques. Composition profiles obtained by AES indicated that the films were stoichiometric to within the accuracy of the technique and uniform in composition; no impurities were detected within the sensitivity of the measurement, approximately 0.1%. C-V measurements on a number of films deposited on Si showed that a number of the films had good dielectric properties, as indicated by small (< 1 V) flat band shifts. By contrast, our earlier $Si_3N_4$ films showed flat band voltage shifts as large as 25 V.

Figure 4 shows the thickness and refractive index of a film deposited at 400°C as a function of position on the substrate; the center of the scan corresponds to the irradiated portion of the surface. The increase in refractive index and the decrease in thickness in the irradiated region indicate that densification has taken place. A tentative explanation of the effect is that the UV radiation increases the mobility of species deposited on the substrate, leading to a denser film. The observation suggests that UV irradiation may be a useful technique in reducing the temperatures required for thin-film deposition.

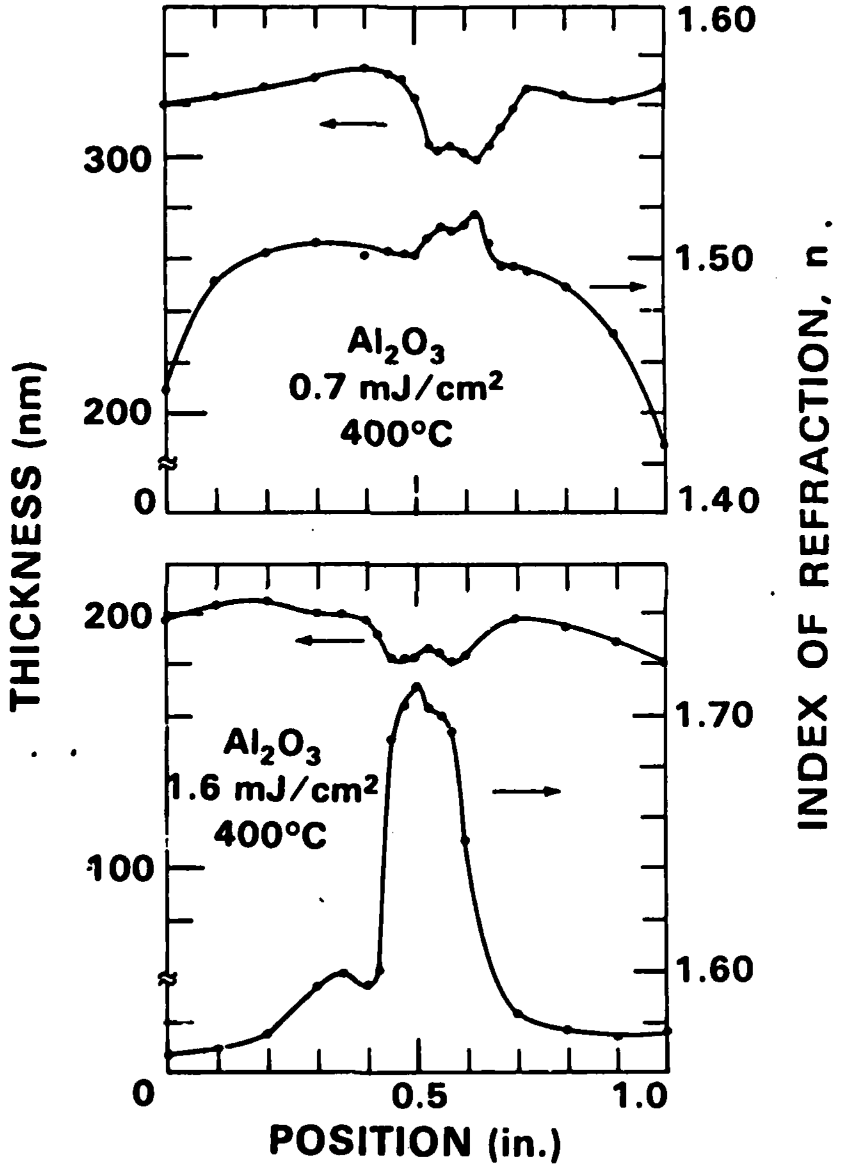

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Fig. 4. Variation of refractive index and thickness of UV-irradiated $Al_2O_3$ as a function of position on the substrate for two different irradiation levels. The irradiated region is approximately at the center of the scan.

## Meeting Speeches and Publications (cumulative)

T. F. Deutsch, D. J. Ehrlich and R. M. Osgood, Jr., "Laser Photodeposition of Metal Films with Microscopic Features," Appl. Phys. Lett. 35, 175 (1979).

T. F. Deutsch, D. J. Ehrlich and R. M. Osgood, Jr., "Laser Initiated Deposition of Metal Films with Microscopic Features," 1979 IEEE/OSA Conference on Laser Engineering and Applications Technical Digest, Paper 7.1.

D. J. Ehrlich, R. M. Osgood, Jr. and T. F. Deutsch, "Laser-Induced Microscopic Etching of GaAs and InP," Appl. Phys. Lett. 36, 698 (1980).

T. F. Deutsch, D. J. Ehrlich, R. M. Osgood, Jr. and Z. L. Liau, "Ohmic Contact Formation on InP by Pulsed Laser Photochemical Doping," Appl. Phys. Lett. 36, 916 (1980).

D. J. Ehrlich, R. M. Osgood, Jr. and T. F. Deutsch, "Direct Writing of Regions of High Doping on Semiconductors by UV-Laser Photodeposition," Appl. Phys. Lett. 36, 916 (1980).

D. J. Ehrlich, T. F. Deutsch and R. M. Osgood, Jr., "Laser Induced Photochemical Reactions for Electronic Device Fabrication," Laser and Electron Beam Processing of Materials, edited by C. W. White and P. S. Peercy (Academic Press, New York, 1980), p. 671.

T. F. Deutsch, D. J. Ehrlich and R. M. Osgood, Jr., "Laser Photochemical Techniques for Semiconductor Processing," CLEOS '80 Technical Digest, Paper ThJJ2.

D. J. Ehrlich, R. M. Osgood, Jr. and T. F. Deutsch, "Laser Microphotochemistry for Use in Solid State Electronics," IEEE J. Quantum Electron. QE-16, 1233, (1980).

D. J. Ehrlich, R. M. Osgood, Jr., D. J. Silversmith and T. F. Deutsch, "One-Step Repair of Transparent Defects in Hard-Surface Photolithographic Masks Via Laser Photodeposition," Electron Device Lett. EDL-1, 101 (1980).

D. J. Ehrlich, R. M. Osgood, Jr. and T. F. Deutsch, "Direct Writing of Micrometer-Sized, Highly Doped Regions on Semiconductors by UV Laser Photodeposition," Paper presented at Device Research Conference, June, 1980.

D. J. Ehrlich, R. M. Osgood, Jr. and T. F. Deutsch, "Laser-Induced Microchemistry," XI International Quantum Electronics Conference, Digest of Technical Papers, Paper C-9, Boston, Massachusetts, June, 1980.

R. M. Osgood, Jr., D. J. Ehrlich and T. F. Deutsch, "Direct-Write Laser Processing for Microelectronics," VLSI Symposium, MIT, 7 October 1980.

D. J. Ehrlich, R. M. Osgood, Jr. and T. F. Deutsch, "Origins of High Spatial Resolution in Photochemical, Direct-Write Laser Processing," Materials Research Society Annual Meeting, Boston, Massachusetts, 16-21 November 1980.

T. F. Deutsch, J. C. C. Fan, G. W. Turner, R. L. Chapman, D. J. Ehrlich, and R. M. Osgood, Jr., "Efficient Si Solar Cells by Laser Photochemical Doping," Appl. Phys. Lett. 38, 144 (1981).

D. J. Ehrlich, R. M. Osgood, Jr. and T. F. Deutsch, "Laser Photochemical Microalloying for Etching of Aluminum Thin Films," Appl. Phys. Lett. 38, 399 (1981).

T. F. Deutsch, R. M. Osgood, Jr. and D. J. Ehrlich, "Laser Microchemistry: Applications in Semiconductor Processing," Physics News in 1980 (AIP), 70 (1980).

D. J. Ehrlich and R. M. Osgood, Jr., "UV Photolysis of Van der Waals Molecular Films," Chem. Phys. Lett. 79, 381 (1981).

D. J. Ehrlich, R. M. Osgood, Jr. and T. F. Deutsch, "Spatially Delineated Growth of Metal Films Via Photochemical Prenucleation," Appl. Phys. Lett. 38, 946 (1981).

D. J. Ehrlich, R. M. Osgood, Jr., and T. F. Deutsch, "Laser Chemical Technique for Rapid Direct Writing of Surface Relief in Silicon," Appl. Phys. Lett. Appl. Phys. Lett. 38, 1018 (1981).

D. J. Ehrlich, R. M. Osgood, Jr., and T. F. Deutsch, "Direct Writing of Refractory Metal Thin Film Structures by Laser Photodeposition," J. Electrochem. Soc. 128, 2041 (1981).

D. J. Ehrlich, R. M. Osgood, Jr., and T. F. Deutsch, "Laser Microreaction for Deposition of Doped Silicon Films," Appl. Phys. Lett. 39, 957 (1981).

John C. C. Fan, T. F. Deutsch, G. W. Turner, D. J. Ehrlich, R. L. Chapman and R. M. Osgood, Jr., "A New Technique for Preparing p-n Junctions for Si Photovoltaic Cells," Proceedings of the 15th IEEE Photovoltaic Specialists Conference, June, 1981, p. 432.

T. F. Deutsch, D. J. Ehrlich, G. W. Turner, J. C. C. Fan, and R. M. Osgood,Jr., "Pulsed UV Laser Photochemical Doping of Semiconductors," CLEO '81 Technical Digest, Paper THH4, Washington, D.C. June 1981.

D. J. Ehrlich, R. M. Osgood, Jr., and T. F. Deutsch, "Laser Photochemistry at Surface for Applications in Microelectronics," CLEO '81 Technical Digest, Paper THH5, Washington, D.C. June 1981.

T. F. Deutsch, D. J. Ehrlich, D. D. Rathman, D. J. Silversmith, and R. M. Osgood, Jr., "Electrical Properties of Laser Chemically Doped Silicon," Appl. Phys. Lett. 39, 825 (1981).

D. J. Ehrlich, R. M. Osgood, Jr., and T. F. Deutsch, "Ultraviolet Photochemical Processing," talk at Electronic Materials Conference, Santa Barbara, CA, June 1981.

D. J. Ehrlich, R. M. Osgood, Jr., and T. F. Deutsch, "Rapid Direct Writing of Surface Relief Structures in Silicon Using Laser Photoetching," talk at Device Research Conference, Santa Barbara, CA, June 1981.

R. M. Osgood, Jr., A. Sanchez-Rubio, D. J. Ehrlich, and V. Daneu, "Localized Laser Etching of Compound Semiconductors in Aqueous Solution," Appl. Phys. Lett. 40, 391 (1982).

D. J. Ehrlich and R. M. Osgood, Jr., "Laser Microchemistry: Local Nucleation Mechanisms for Photodeposition," submitted to Thin Solid Films.

D. J. Ehrlich, R. M. Osgood, Jr., and T. F. Deutsch, "Photodeposition of Metal Films with Ultraviolet Light," J. Vac. Sci. and Tech. 21, 23 (1982).

D. J. Ehrlich, R. M. Osgood, Jr., and T. F. Deutsch, "Laser Microchemistry for Electronics," Invited Talk at 5th International Thin Films Congress, Haifa, Israel, September, 1981.

V. Daneu, R. M. Osgood, Jr., and D. J. Ehrlich, "Optical Reflectance Technique for Observations of Submonolayer Adsorbed Films," Optics Lett. 6, 563 (1981).

T. F. Deutsch, John C. C. Fan, D. J. Ehrlich, G. W. Turner, R. L. Chapman, and R. P. Gale, "Efficient GaAs Solar Cells Formed by UV Laser Chemical Doping," Appl. Phys. Lett. 40, 722 (1982).

D. J. Ehrlich, D. J. Silversmith, R. W. Mountain, and J. Y. Tsao, "Fabrication of Through-Wafer Via Conductor in Si by Laser Photochemical Processing," to be published in IEEE Transactions on Components, Hybrids, and Manufacturing Technology.

J. Y. Tsao, D. J. Ehrlich, D. J. Silversmith, and R. W. Mountain, "Direct-Write Metallization of Si MOSFETs Using Laser Photodeposition," Electron Device Lett. EDL-3, 164 (1982).

D. J. Ehrlich and J. Y. Tsao, "Submicrometer-linewidth Doping and Relief Definition in Silicon by Laser-controlled Diffusion," Appl. Phys. Lett. 41, 297 (1982).

D. J. Ehrlich, T. F. Deutsch, R. M. Osgood, Jr., and D. J. Silversmith, "Laser Photochemical Processing for Microelectronics," in Proceedings of the 14th Conference (1982 International) on Solid State Devices, Tokyo, 1982: Jpn. J. Appl. Phys. 22, Supp. 22-1, 161 (1983).

S. R. J. Brueck and D. J. Ehrlich, "Stimulated Surface-Plasma-Wave Scattering and Growth of a Periodic Structure in Laser-Photodeposited Metal Films," Phys. Rev. Lett. 48, 1678 (1982).

D. J. Ehrlich, S. R. J. Brueck, and J. Y. Tsao, "Time-Resolved Measurements of Stimulated Surface Polariton Wave Scattering and Grating Formation in Pulsed-Laser-Annealed Germanium," Appl. Phys. Lett. 41, 630 (1982).

J. Y. Tsao and D. J. Ehrlich, "Submicrometer-Linewidth Laser Doping." in Laser Diagnostics and Photochemical Processing Semiconductor Devices, edited by R. M. Osgood, Jr., S. R. J. Brueck, and H. R. Schlossberg (North-Holland, New York, 1983), p. 235.

D. J. Ehrlich and J. Y. Tsao, "Laser Fabrication of Microstructures: Effect of Geometric Scaling on Chemical Reaction Rates," in Laser Diagnostics and Photochemical Processing Semiconductor Devices, edited by R. M. Osgood, Jr., S. R. J. Brueck, and H. R. Schlossberg (North-Holland, New York, 1983), p. 3.

D. J. Ehrlich, D. J. Silversmith, R. W. Mountain, and J. Y. Tsao, "Fabrication of Through-Wafer Via Conductors in Si by Laser Photochemical Processing," IEEE Trans. Parts., Hybrids, Packaging CHMT-4, 520 (1982).

T. F. Deutsch, D. J. Silversmith, and R. W. Mountain, "UV Laser Initiated Formation of $Si_3N_4$," in Laser Diagnostics and Photochemical Processing Semiconductor Devices, edited by R. M. Osgood, Jr., S. R. J. Brueck, and H. R. Schlossberg, (North-Holland, New York, 1983), p. 129.

T. F. Deutsch, "Pulsed UV Excimer Laser Doping of Semiconductors," in Laser Diagnostics and Photochemical Processsing Semiconductor Devices, edited by R. M. Osgood, Jr., S. R. J. Brueck, and H. R. Schlossberg, (North-Holland, New York, 1983), p. 225.

J. Y. Tsao, R. A. Becker, D. J. Ehrlich, and F. J. Leonberger, "Photodeposition of Ti:$LiNbO_3$ Waveguides," Appl. Phys. Lett. 42, 559 (1983).

M. W. Geis, J. N. Randall, T. F. Deutsch, P. D. DeGraff, K. E. Krohn, and L. A. Stern, "Self-Developing Resist with Submicrometer Resolution and Processing Stability," Appl. Phys. Lett. 43, 74 (1983).

T. F. Deutsch and M. W. Geis, "Self-Developing UV Photoresist Using Excimer Laser Exposure," to be published in J. Appl. Phys.

J. Y. Tsao and D. J. Ehrlich, "UV Laser Photopolymerization of Volatile Surface-Adsorbed Methyl Methacrylate," Appl. Phys. Lett. 42, 997 (1983).

D. J. Ehrlich, S. R. J. Brueck, and J. Y. Tsao, "Surface Electromagnetic Waves in Laser-Surface Interactions," in Laser Diagnostics and Photochemical Processing Semiconductor Devices, edited by R. M. Osgood, Jr., S. R. J. Brueck, and H. R. Schlossberg, (North-Holland, New York, 1983).

D. J. Ehrlich and J. Y. Tsao, "Laser Direct Writing for VLSI," to be published in VLSI Electronics: Microstructure Science, Vol. 9, edited by N. G. Einspruch, (Academic Press, New York, 1983).

D. J. Ehrlich and J. Y. Tsao, "A Review of Laser Direct Writing," submitted to J. Vac. Sci. Technol.

D. J. Ehrlich and J. Y. Tsao, "Laser Photoreactions of Volatile Surface-Adsorbed Molecules," in Surface Studies with Lasers, edited by F. R. Aussenegg, A. Leitner, and M. E. Lippitsch (Springer-Verlag, Berlin, 1983).

J. Y. Tsao and D. J. Ehrlich, "Laser-Controlled Chemical Etching of Aluminum," Appl. Phys. Lett. 43, 146 (1983).

# Self-developing resist with submicrometer resolution and processing stability

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Nitrocellulose films have been shown to function as self-developing resist layers that are sensitive to both low-energy ($<2$ keV) $Ar^+$ ions and to 193-nm UV radiation from pulsed excimer lasers. A resolution of $<100$ nm and aspect ratios $>25:1$ have been demonstrated using a stencil mask and an argon ion beam; the resolution obtained was mask limited. The sensitivity of the resist to 2-keV $Ar^+$ ions is 36 $\mu$m/min at beam currents of 1 mA/cm$^2$, allowing exposure times of 1 s for 0.5 $\mu$m of resist. The material is capable of functioning as a mask material for typical semiconductor dry etching processes.

PACS numbers: 79.20.Nc, 79.20.Ds, 82.50.Et, 82.50.Rf

Self-developing resists are a class of materials which volatilize during exposure to radiation, eliminating the need for a subsequent development step. Several groups have reported on materials which can be used as self-developing resists when exposed to appropriate radiation.[1-7] These resists often have several processing difficulties such as low sensitivity,[2] formation of nonvolatile residues,[1,6] and poor stability.[6,7] In this letter we report the first use of nitrocellulose as a self-developing resist which exhibits both sensitivity comparable to commonly used resists and sufficient processing stability to be used as a mask material for typical semiconductor dry etching processes. Nitrocellulose has been used previously as a conventional resist requiring a solvent for development[8] and as an ablative recording medium for video disks.[9] To our knowledge, this is the first report of a self-developing ion-beam resist. Many self-developing resists which exhibit useful sensitivity, like poly(butene-1 sulfone) (PBS), rely upon "weak" chemical bonds which break during radiation, decomposing the polymer resist into its volatile monomers.[1] However, nitrocellulose is a polymer with comparatively "strong" chemical bonds. The self-developing properties arise from chemical reactions between oxidizing groups, $NO_3$, and reducing groups, CH, which produce volatile products such as CO, $CO_2$, $H_2O$, $H_2$, and $N_2$.[10] This resist is sensitive to ion beams and UV radiation and has demonstrated resolution better than 100 nm. In addition, the self-developing property of the resist makes it possible to obtain aspect ratios $>25:1$ (i.e., ratios of resist thickness to minimum linewidth).

Nitrocellulose linen fibers with 13.2% nitrogen content[11] were dissolved in amyl acetate, $CH_3(CH_2)_4OOCCH_3$, yielding solutions with nitrocellulose concentrations varying from 1% to 10% by weight; a 0.2-$\mu$m filter was used to remove undissolved fibers. The nitrocellulose solution was spun on silicon wafers and the residual solvent was removed by baking at 80 °C for 30 min in a flowing $N_2$ atmosphere. This produced films whose thickness could be varied from 0.05 to 20 $\mu$m by changing the solution viscosity and the spin speed.

Ion beam exposures were made in a cryopumped vacuum system which was pumped to a pressure of $1\times10^{-6}$ Torr before back filling with argon to a chamber pressure of $2\times10^{-4}$ Torr. The argon was injected through a 10-cm Kaufman ion source and a plasma bridge neutralizer.[12] The resist samples were normally maintained within a few degrees of room temperature by heat sinking them to a water-cooled block with a conductive thermal grease. Figure 1(a) shows the etch rate for argon ions, normalized to a beam current of 1 mA/cm$^2$, as a function of ion energy. For samples held at room temperature the etch rate is proportional to ion flux density and independent of time. However, as shown in Fig. 1(b) the etch rate is dependent upon the sample temperature. These results were obtained by mounting the sample on a strip heater. The decrease in development rate with

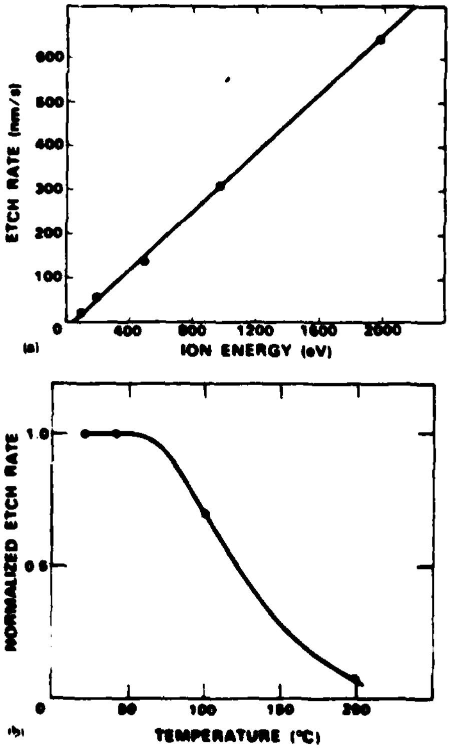

FIG. 1. (a) Etch rate of nitrocellulose as a function of argon ion energy. The data are normalized to a beam current of 1 mA/cm$^2$. (b) Normalized etch rate of nitrocellulose as a function of substrate temperature. A beam of 500-eV argon ions was used at a flux density of 30 $\mu$A cm$^{-2}$.

# Laser-controlled chemical etching of aluminum

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(Received 9 March 1983; accepted for publication 3 May 1983)

A new technique is described for high-spatial-resolution ( $< 2$-$\mu$m linewidth) etching of Al thin films. The process is based upon moderate local heating by a tightly focused $Ar^+$ laser beam to activate an etching reaction in mixtures of phosphoric acid, nitric acid, and potassium dichromate. By chemically biasing the reaction near its passive/active transition, the laser can enhance the reaction rate by more than six orders of magnitude. The etching mechanism has been studied by etch-rate measurements, ellipsometry, and Auger spectroscopy, and is ascribed to a competition between the formation of soluble aluminum phosphates and insoluble aluminum oxides.

PACS numbers: 81.60.Bn, 68.20. + t, 82.45. + z, 79.20.Ds

Recently, there has been growing interest in laser-controlled chemical processes for microfabrication. For example, such processes have been used to locally etch semiconductors[1] and ceramics.[2] Developing a similar technique for controllably etching a metal such as aluminum has been complicated, however, by the vastly different chemical reactivities between the metal and its passivating surface oxide. The etch resistance of this oxide is the source of considerable variability for all current techniques of wet and dry Al etching. In this letter we describe a new process for laser-enhanced Al etching in which the chemical passivity of the oxide is turned to an advantage. The process uses solutions based upon nitric acid, a strong oxidizer, and phosphoric acid, which reacts with Al ions to form soluble aluminum phosphates. Its mechanism, based on a thermal modification of a kinetic balance between the interfacial reactions which form and dissolve this oxide layer, is distinct from those of previous techniques for laser-enhanced etching in electrolytes, based either on photogenerating carriers in semiconductors[1] or on increasing material transport into or out of a strongly heated reaction zone.[2] It is also distinct from a two-step photochemical microalloying/etching technique that has been previously described[3]; this is the first laser technique that etches Al thin films in one step.

The new technique has several practical advantages over existing laser-ablative methods with respect to resolution, control, and greatly reduced process temperature. Although requiring substrate immersion in a wet etchant, the etchant has been optimized to be extemely noncorrosive at ambient temperature. Consequently, it may be widely useful for removing excess Al left by random patterning errors in integrated-circuit fabrication and for cutting links on redundant or custom circuitry. To demonstrate this, we have made laser exposures of integrated-circuit metallization patterns using a cw $Ar^+$ laser combined with a high-magnification optical microscope both to focus the laser beam onto the substrate and to allow *in situ* viewing of the etching process. Figure 1 shows scanning electron micrographs of a laser etched cut in a 200-nm-thick conductor and, for comparison, a conductor partially disrupted by irradiation in air. Four shuttered, 100-ms laser pulses were used in each case; however, the power level required for chemical etching is $\sim 0.12$ W, whereas that required for complete ablation in air is $\sim 0.4$–$0.5$ W. Based on cross calibrations the peak temperature during etching is estimated to be $\sim 200$ °C. Equivalent results were obtained with unsintered and sintered films of both Al and $Al_{0.95}Cu_{0.04}Si_{0.01}$. The improved edge control and spatial resolution associated with chemical etching is significant; a minimum width of $\sim 1.5$ $\mu$m was demonstrated here for 0.2-$\mu$m-thick metal films on 1-$\mu$m-thick $SiO_2$ on Si wafers. The high spatial resolution possible for such thermally activated reactions, even on good thermal conductors, has been discussed previously.[4]

In order to optimize the system for laser-enhanced etching, and to understand its mechanism, we have characterized the unilluminated-reaction rates over a range of solution compositions and temperatures, and have directly measured the dielectric-surface-layer thickness and compo-

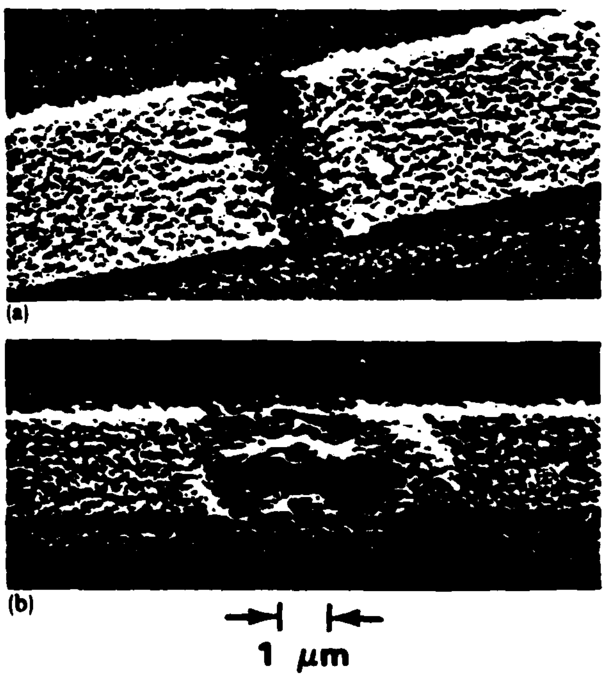

FIG. 1. Scanning electron micrographs (a) of a cut in 0.2-$\mu$m-thick Al circuit metallization using laser-controlled etching (four 0.12-W, 100-ms pulses); and (b) of a threshold-power disruption of the same metallization in air (four 0.39-W, 100-ms pulses). Higher powers are needed for complete ablation. The substrate is Si covered by a 1-$\mu$m thermally grown oxide.

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# SELF-DEVELOPING UV PHOTORESIST USING EXCIMER LASER EXPOSURE

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## ABSTRACT

Nitrocellulose functions as a self-developing photoresist which can be patterned using pulsed excimer laser radiation. The material exhibits a threshold fluence for ablation of 20 mJ/cm$^2$ at a wavelength of 193 nm; this threshold results in higher contrast than can be obtained with most conventional photoresists. The effect of varying the laser wavelength has been examined. A simple model of ablative development has been used to predict the etch rate. The processing stability of the resist has been increased without changing the optical development rate by the addition of a dopant. The resolution of the resist is better than 0.3 μm.

We have recently reported that nitrocellulose can function as a self-developing resist sensitive to both low-energy ion beams and to 193 nm UV excimer laser radiation; the results of the laser experiments were only summarized briefly.[1] Here we report on the properties of nitrocellulose as a UV resist material which has higher contrast than most conventional photoresists, exhibits submicrometer resolution, and has properties compatible with many semiconductor processing operations. The effect of varying the laser wavelength has been examined and can be understood in terms of the optical absorption of the resist. A simple model of ablative development, applicable to any self-developing resist showing a threshold, has been used to give the etch rate near threshold. The use of additives to alter the properties of the resist in subsequent processing steps without reducing the optical sensitivity has been demonstrated. A resolution of at least 0.3 μm, substantially higher than previously reported, has been demonstrated.

The self-developing property of the resist results from the fact that it can be decomposed into volatile products by sufficiently intense UV irradiation; similar excimer laser ablation of relatively thick polymer films has been reported by others.[2,3] In addition, the self-developing properties of nitrocellulose are believed to result not just from photolysis into volatile monomers, as is the case for some self-developing resists.[4,5] They result instead from chemical reactions between oxidizing groups, $NO_3$, and reducing groups, CH, which react to produce volatile products such as CO, $CO_2$, $H_2O$, $H_2$, $N_2$, and NO.

Nitrocellulose films having thicknesses ranging from 0.5 to 3 μm were prepared by spinning a solution of nitrocellulose in amyl acetate onto silicon wafers; the details of the procedure have been described previously.[1] Measurements of etch depth were made by using a Sloan Dektak profiler to determine the depth of an approximately 1 mm diam spot made using a weakly focused ArF excimer laser beam. The exposed regions were also examined with an ellipsometer to determine if there was any residue; less than 3 nm was found.

Figure 1a shows the etch rate of nitrocellulose expressed in terms of thickness removed per unit fluence per pulse as a function of fluence (energy per unit area) at 193 nm. A threshold value for development of approximately 20 $mJ/cm^2$ is observed; since there is a threshold, the resist does not obey reciprocity. That is, the development does not depend only on the total energy dose delivered, as would be the case for a conventional resist. As discussed below, this results in a variable contrast. Below threshold not only is the development rate almost immeasurable, but the exposed region has a rough, textured surface rather than a smooth profile. The etch rate increases with fluence, reaching a maximum at 50 $mJ/cm^2$. Fig. 1b shows the thickness removed per pulse as a function of fluence, along with the predictions of the model presented below.

The development of an ablative resist exhibiting a threshold can be described by a simple model. Development will extend to a thickness, T, at which the incident fluence has been attenuated to the threshold value $E_{th}$. This can be expressed, using Beer's law, by

$$T = \alpha^{-1} \ln (E/E_{th}) \qquad (1)$$

where $\alpha$ is the absorption coefficient of the resist. The initial portion of the experimental data in Fig. 1b can be fitted using this expression. The value of $\alpha^{-1}$ obtained from the fit, 78 nm, is in good agreement with a value of 80 nm obtained from transmission measurements. Above about 0.1 $J/cm^2$, the observed values of T are greater than predicted. This is probably due to the release of the energy of explosion, about 40 $eV/nm^3$, by the nitrocellulose, since resists with endothermic decomposition products show no such increase.[6] The functional form given by Equation (1) would be expected to describe the development of any resist showing a threshold and has indeed been observed in the ablative development of other polymer materials.[2,3]

The energy per unit volume deposited at threshold can be predicted if one assumes development will start when there is one incident 6.4 eV ArF laser photon per ring structure in the nitrocellulose monomer; there are two such six-carbon rings per monomer molecule. From the handbook values of the density and molecular weight of the nitrocellulose monomer one finds that there are 1.7 monomer molecules/nm$^3$. The energy deposition per unit volume is then 22 eV/nm$^3$. From Eq. (1), the calculated energy deposition at threshold is

$$dE/dT \Big|_{T=0} = E_{th}\,\alpha \qquad (2)$$

The values of $E_{th}$ and $\alpha$ used to fit the data of Fig. 1b to Equation (1) give an energy deposition of 12 eV/nm$^3$ at threshold, in reasonable agreement with the calculated value, and with the assumption that each photon leads to the dissociation of a ring structure.

The effect of the fluence-dependent etch rate on the contrast can best be understood by using the curve of Fig. 1a to calculate the development of a 1000-nm-thick film of nitrocellulose using 5, 10, and 30 laser shots. The results are shown in Fig. 2; note that total dose is plotted on the abscissa. The contrast, $\gamma$, is given by the expression:

$$\gamma = [\log_{10} D_{1000}/D_0]^{-1} \qquad (3).$$

Here $D_{1000}$ and $D_0$ are the doses required to ablate 1000 nm and to just begin ablation, respectively. As the number of shots used to expose the film increases, the energy per pulse decreases, approaching threshold, and the contrast increases. The contrast of 7 obtained using 30 shots to develop the film is higher than that obtained using lamp exposure of most conventional photoresists, which typically have contrasts between 1 and 3.

Patterns were also produced using 248 nm KrF and 351 nm XeF laser radiation; however, the morphology of the exposed region was different than with 193 nm radiation, with numerous fibrous filaments visible. The reason for this is believed to be heating of the silicon substrate by the laser radiation. In contrast to 193 nm, where the absorption length is 80 nm and the incident radiation is almost entirely absorbed in the nitrocellulose, at 248 nm the absorption length is 6 μm and significant amounts of energy reach the substrate. We have also exposed PMMA (polymethylmethacrylate) using both 193 and 248 nm radiation; in this case, even the 193 nm exposures were fibrous and, therefore, undesirable for submicrometer structures; the absorption length of PMMA was measured to be 2.4 μm at 193 nm, again indicating substrate heating.

Fig. 3 (top) shows a grating pattern in nitrocellulose produced using a 3.8-μm-period grating mask contacted to the substrate; the pattern in Fig. 3 (bottom) was produced by spacing the mask about 40 μm from the substrate. It has previously been demonstrated that under similar conditions diffraction effects can result in spatial intensity patterns, having periods 1/N that of the original mask (N=integer), occurring away from the mask.[7,8] The pattern in Fig. 3 (bottom) is due to this phenomenon, called spatial period division, and serves to illustrate that the resolution of the resist is ~0.3 μm.

Difficulty can be encountered with contact mask lithography due to the volatile products which form during exposure, causing the mask and the substrate to separate. In order to examine the resolution limits of the resist further, we utilized the diffraction from the edge of a cleaved, 100-μm-thick Si wafer contacted to a 0.6-μm-thick nitrocellulose film on a Si substrate. Figure 4 shows an optical micrograph of the resulting pattern. The grating lines extend to the resolution limit of the microscope. Scanning electron microscope studies of this pattern show incompletely developed line pairs spaced as close as 0.25 μm apart. This spacing is approximately ten times closer than previously reported for an optical self-developing resist.[2] The micrograph also serves to illustrate the high contrast of the resist, since the intensity pattern of diffraction from an edge consists of a relatively weak modulation about an average light intensity rather than the 100% modulation that is obtained using a mask pattern. The calculated intensity variation at the edge of the pattern is less than 1% of the average intensity.

The stability of nitrocellulose in a number of typical semiconductor processing operations has been described in an earlier publication.[1] It is possible to add dopants or additives to alter the processing behavior of nitrocellulose. For example, the addition of 10%, by weight, of ferrocene to the nitrocellulose results in a factor of four reduction in the etch rate under typical conditions for reactive ion etching of $SiO_2$ (25 Torr $CHF_3$ at 45 sccm) while leaving the sensitivity to optical radiation unchanged. By contrast, the sensitivity to ion beam exposure was reduced by a factor of twenty by the doping, indicating a difference between the development mechanisms for optical and ion exposure. Similarly, additives which have strong UV absorptions may be useful sensitizers with polymers like PMMA which have relatively low UV absorption coefficients.

We have described some of the properties of the self-developing UV resist, nitrocellulose. The development of the material at fluence values near threshold can be explained by a simple model which is applicable to any material showing a threshold; the non-reciprocal behavior of the resist results in higher contrasts than are generally available.

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## REFERENCES

1. M. W. Geis, J. N. Randall, T. F. Deutsch, P. D. DeGraff, K. E. Krohn, and L. A. Stern, Appl. Phys. Lett. 43, 74 (1983).

2. R. Srinivasan and V. Mayne-Banton, Appl. Phys. Lett. 41, 576 (1982).

3. J. E. Andrew, private communciation.

4. L. F. Thompson and M. J. Bowden, J. Electrochem. Soc. 120, 1722 (1973).

5. M. J. Bowden, CRC Crit. Rev. Solid State Sci. 8, 223 (1978).

6. R. Srinivasan, private communication.

7. D. C. Flanders, A. M. Hawryluk, and H. I. Smith, J. Vac. Soc. Technol. 6, 1949 (1979).

8. A. M. Hawryluk, H. I. Smith, R. M. Osgood, Jr., and D. J. Ehrlich, Opt. Lett. 7, 402 (1982).

## FIGURE CAPTIONS

Figure 1. (a) Development rate per pulse for nitrocellulose versus incident 193 nm energy per unit area.

(b) Total development per pulse for nitrocellulose versus energy per unit area.

Figure 2. Calculated development of a 1000-nm-thick nitrocellulose film as a function of total 193 nm dose for 5, 10, and 30 shot irradiations. The effective contrast, $\gamma$, for each irradiation condition is given. The curve is calculated from the data of Fig. 1(a).

Figure 3. (Top) Optical micrograph of a grating pattern in nitrocellulose obtained using 193 nm ArF laser radiation and a 3.8 μm period chrome-on-quartz mask contacted to the Si substrate.

(Bottom) Grating pattern obtained when the mask is spaced away from the substrate in order to obtain spatial period division effects (see text).

Figure 4. Optical micrograph of a grating pattern in nitrocellulose produced by diffraction from the edge of a 100-μm-thick Si wafer contacted to the substrate.

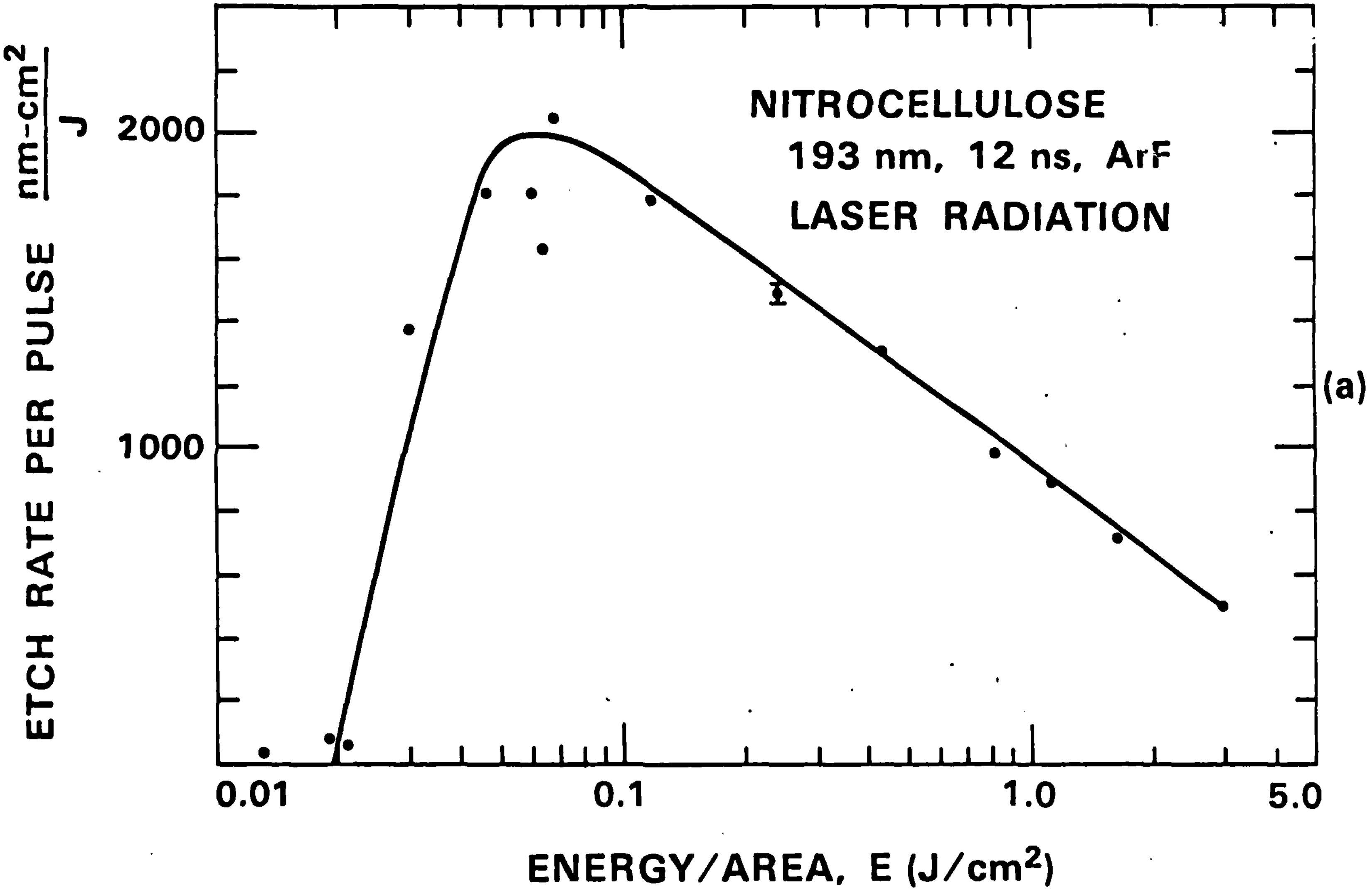

Fig. 1

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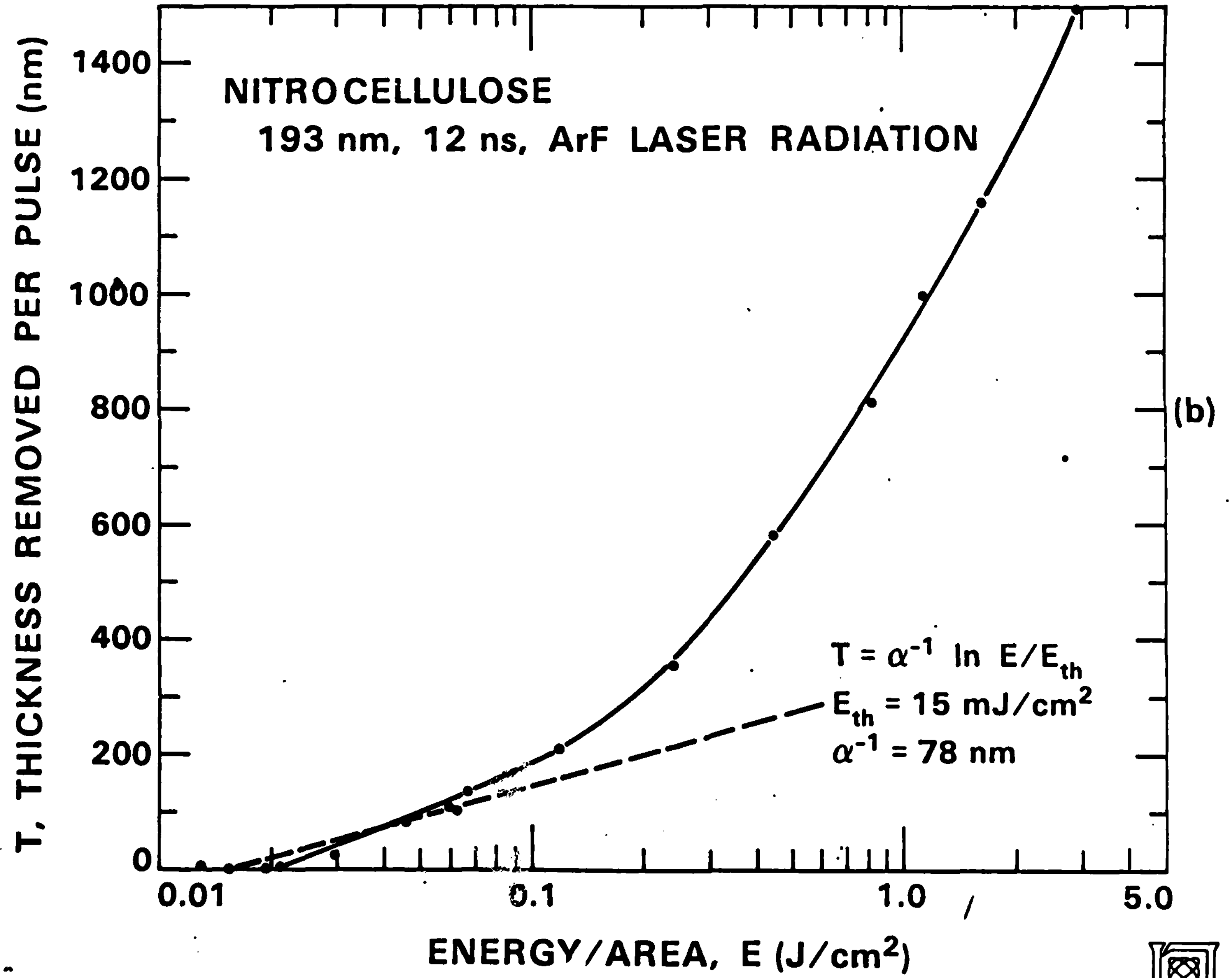
NITROCELLULOSE
193 nm, 12 ns, ArF LASER RADIATION
T, THICKNESS REMOVED PER PULSE (nm)
0
200
400
600
800
1000
1200
1400
ENERGY/AREA, E (J/cm$^2$)
0.01
0.1
1.0
5.0
$T = \alpha^{-1} \ln E/E_{th}$
$E_{th} = 15 \text{ mJ/cm}^2$
$\alpha^{-1} = 78 \text{ nm}$
(b)

Fig. 1(b)

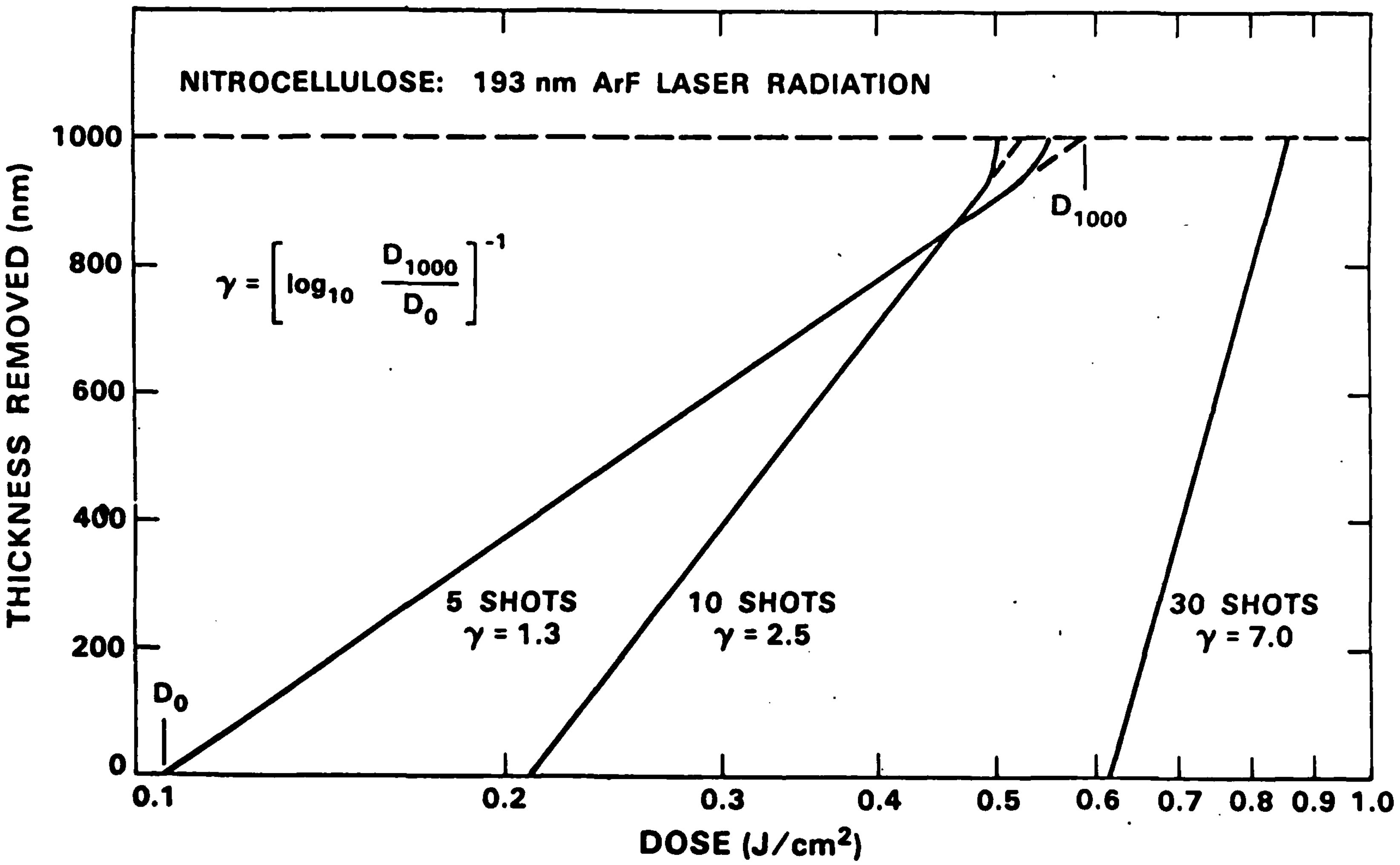
NITROCELLULOSE: 193 nm ArF LASER RADIATION
$\gamma = \left[\log_{10} \frac{D_{1000}}{D_0}\right]^{-1}$
$D_{1000}$
$D_0$
5 SHOTS
$\gamma = 1.3$
10 SHOTS
$\gamma = 2.5$
30 SHOTS
$\gamma = 7.0$
THICKNESS REMOVED (nm)
1000
800
600
400
200
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
DOSE ($J/cm^2$)

FIGURE 2

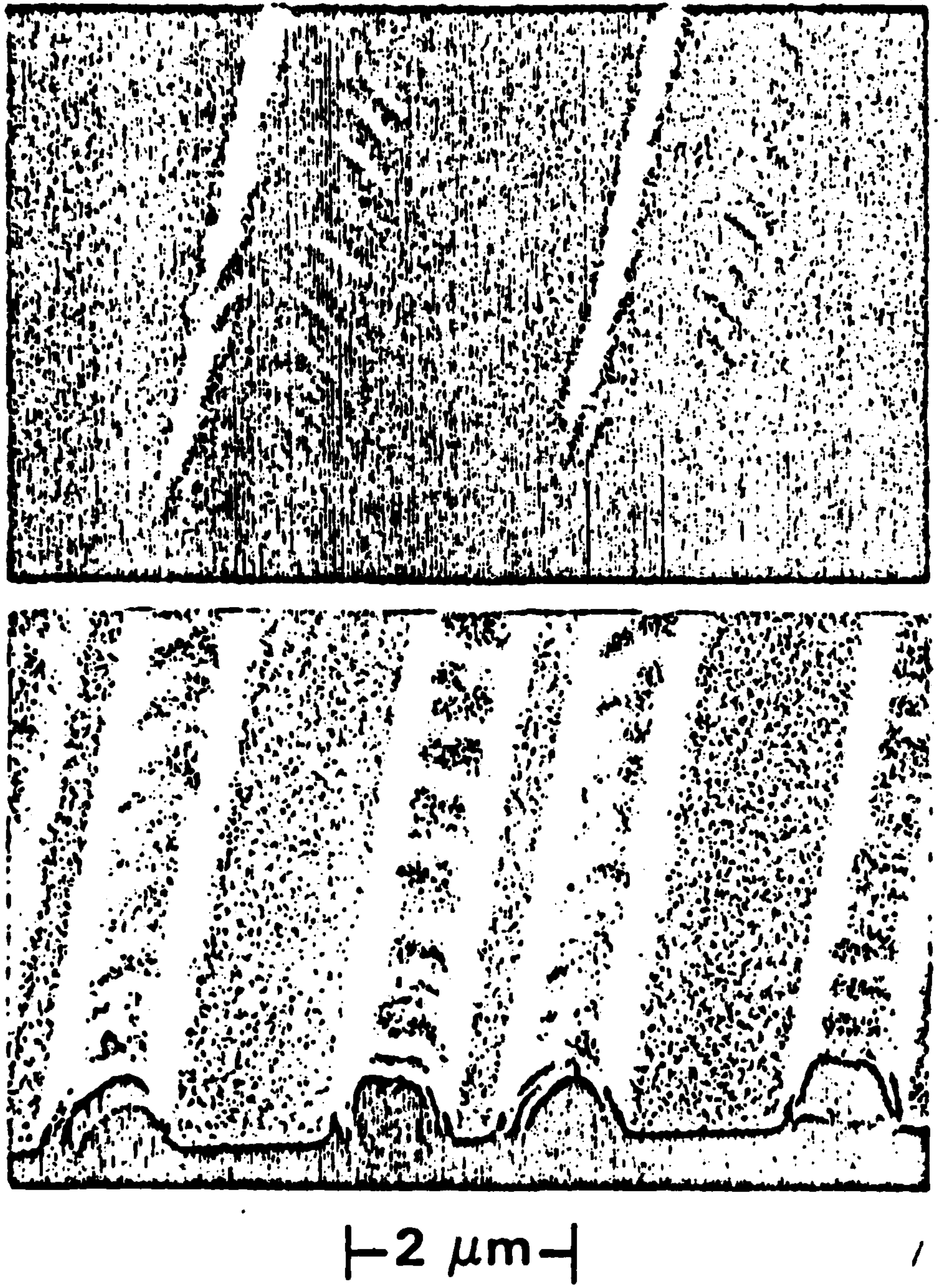

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Fig. 3

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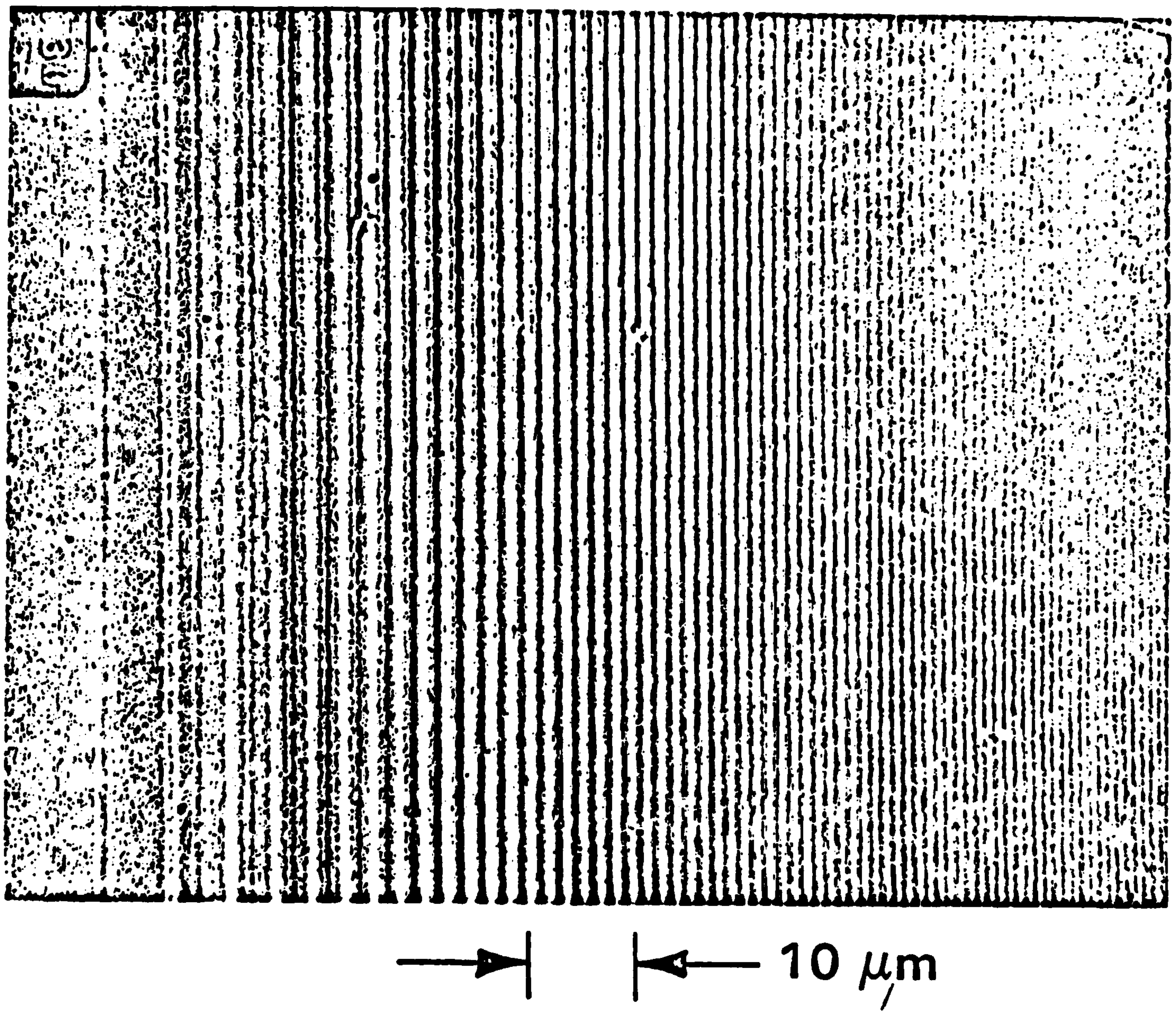

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Fig. 4

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Nitrocellulose films have been shown to function as self-developing resist layers that are sensitive to both low-energy ($< 2$ keV) $Ar^+$ ions and to 193-nm UV radiation from pulsed excimer lasers. A resolution of $< 100$ nm and aspect ratios $> 25:1$ have been demonstrated using a stencil mask and an argon ion beam; the resolution obtained was mask limited. The sensitivity of the resist to 2-keV $Ar^+$ ions is 36 $\mu$m/min at beam currents of 1 mA/cm$^2$, allowing exposure times of 1 s for 0.5 $\mu$m of resist. The material is capable of functioning as a mask material for typical semiconductor dry etching processes.

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