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Submicrometer patterning by projected excimer-laser-beam induced chemistry^{a)}

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Projection imaging with the deep-UV (193 nm) and vacuum ultraviolet (VUV) (157 nm) output of an excimer laser has been applied to submicrometer patterning of thin films by injected-defect, surface-chemical, and solid-transformation processing. The methods have been designed to take advantage of the short-wavelength, high-peak-intensity pulsed radiation from these sources. Examples are described of pattern definition by exposure of multilayer organic resists, by maskless etching and doping of solids in reactive vapors, and by solid-state chemical transformations in inorganic Al/O films. Well-resolved 0.4- μm lines and spaces have been achieved. Required doses, between 0.04 and 1 J/cm², are compatible with single- or multipulse step-and-repeat projection patterning with a small excimer laser.

I. INTRODUCTION

Laser-activated surface chemistry is presently being rapidly developed for microelectronics applications. Two generic classes of processing have been explored most extensively. In one class, unfocused or weakly focused laser beams are used to activate unpatterned, extended-area processing steps, e.g., full-wafer deposition or etching.¹ In the other class, scanned, tightly focused laser beams are used to drive micrometer-scale surface chemistry, fabricating structures by direct writing.²

At the same time, some of the same short-wavelength laser sources have been proposed as replacements for conventional lamp sources in resist-based lithography.³ In particular, step-and-repeat optical projection systems for excimer-laser resist exposure are at the time of this writing being designed in a number of laboratories. Most of the photosensitive thin-film systems studied for such lithography have been based upon adaptations of commonly used organic photoresists.³ Nevertheless, as has been recognized by others, because of their short wavelengths and high peak powers, excimer lasers are much more versatile light sources than lamps, and are able to stimulate thin-film modifications inaccessible to lamp exposure, e.g., ablation of organic resists.⁴

In this paper, we describe the application of excimer-laser-activated surface chemistry to projection patterning. Pulsed excimer lasers are particularly attractive for this purpose, since they are at sufficiently short wavelengths to be strongly absorbed by most solids and to efficiently excite electronic-transition photochemistry. Such reactive surface modifications, specifically designed around the short-pulsed nature of excimer sources, may avoid some of the limitations long taken for granted with traditional organic-resist-based lithography. For example, the optimization of resists for use with lamp sources is limited, especially at short wavelengths, by a need to maximize radiation sensitivity. This and other practical considerations limit the range of acceptable materials and the optimization of other processing properties.

In contrast, excimer lasers can use an entirely different range of radiation-driven resist or nonresist processes by pattern projections. Processes based on new reactive organic or inorganic thin-film systems can be designed to have higher

contrast than that previously possible, or to have chemical and thermal properties better matched to a particular lithographic application. In addition, since exposure of current resists is limited to wavelengths greater than 300 nm, the effective use of the shortest excimer wavelengths at 157 and 193 nm would improve resolution even without the new flexibility deriving from the pulsed output.

In the rest of this paper, we discuss these possibilities beyond the traditional photochemical generation of defects in organic polymeric materials. New results demonstrating 0.4- μm lines and spaces will be presented for several systems. Specific systems considered below are those with built-in superlinear (nonreciprocal) intensity responses, and those designed for single-pulse exposure. The former can increase imaging contrast, hence resolution, and can significantly relax the high-spatial-frequency modulation transfer function (MTF) requirements of the projection system. As elaborated below, the latter can relax requirements on vibration isolation, and on the mechanical and operating complexity, of the optical projection system. Somewhat surprisingly, the single-pulse flux requirements of many of the initially selected material systems can already compete with the minimum dose requirements of highly optimized organic resists; most applications are feasible for a small excimer laser and practical step-and-repeat optics.

II. OPTICS

A. General considerations

The UV exposures described here were made using a simple projection system suitable for laboratory experiments. The layout is shown in Fig. 1. For projection lithography, excimer lasers possess some advantages over other sources.³ The output of a small excimer laser, typically in the form of 8–20 ns pulses, has energies of 0.1–1 J/pulse at 193 nm (ArF laser), or several mJ/pulse at 157 nm (F₂ laser). Maximum pulse repetition frequencies are generally 10–10³ pulses/s. The stronger output of 1 J, imaged to the area of a < 1 cm² area integrated-circuit die, permits single-pulse doses of > 1 J/cm². Even if multiple pulses are required, exposure times will potentially be reduced by a large factor relative to deep-UV lamps.

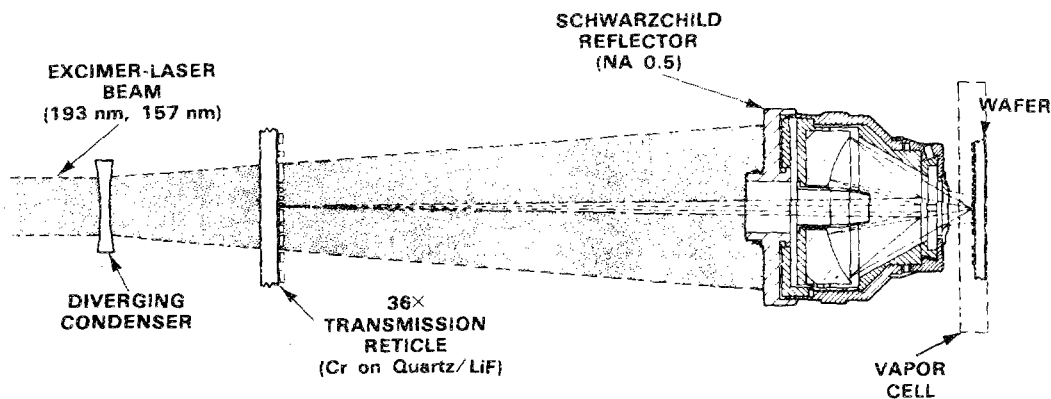


FIG. 1. Laboratory optical system used for UV and VUV excimer projection patterning.

In addition, the high output divergence (> 1 mrad for a nearly planar cavity) and large spectral bandwidth (commonly $100\text{--}200\text{ cm}^{-1}$ in free-running operation) imply low temporal and spatial coherence. As has been found empirically in previous experiments, this causes laser speckle to be unimportant for multipulse exposures. Below we find that speckle is also unimportant for single-pulse exposure.

Excimer laser sources, however, also bring with them a number of difficulties. For example, operation at 193 and 157 nm requires special provision to minimize attenuation due to atmospheric O_2 . In our experiments at 157 nm, the entire beam path was purged with Ar gas. Light at 193 nm can be transmitted through air without unacceptable losses, but atmospheric heating (thermal blooming) and production of ozone due to O_2 dissociation on the tail of the Schumann-Runge absorption cause pulse-to-pulse inhomogeneities and optical distortion. This can also be eliminated with a purged beam path. In addition, because of the UV opacity of fused silica, special masks are required at 157 nm; in our experiments, Cr-on- MgF_2 and Cr-on-LiF masks were used. At 193 nm, more easily fabricated Cr-on-quartz (Suprasil) masks were used. Finally, the short wavelength and partial coherence of excimer sources pose further problems for objective and condenser optics, as discussed below.

B. Objective lens

The optical system for this study makes use of a reflecting, 0.5-numerical-aperture, Schwarzschild, microscope objective lens. There are no refracting elements, making this lens usable at wavelengths (e.g., 157 nm) shorter than the UV transmission cutoff of optical glasses. The lens was used to image a transmission mask near its designed demagnification of $36\times$. By varying the conjugate positions of the mask and image plane, the demagnification can be varied; however, the illumination is not uniform across the image plane for large deviations from the designed demagnification. The most fundamental limitation of this lens as a lithographic tool is its limited ($< 200\ \mu\text{m}$ on a side) field of view. Note that the high demagnification is convenient but not necessary. However, some degree of demagnification is useful to reduce optical intensity at the photomask.

Although this objective has a large numerical aperture and, therefore, transmits some exceptionally high spatial frequencies, it is far from diffraction limited. First, since it was intended primarily for IR imaging, it does not have surfaces figured for the deep UV. Double-pass interferometry in the

visible indicates a wavefront error of ~ 3 UV wavelengths across the central portion of the aperture. Second, the central obstruction of the Schwarzschild design causes a well-known disturbance in the modulation transfer function relative to clear-aperture designs⁵: spatial frequencies in the middle range of the lens are more attenuated, although spatial frequencies near the high-frequency cutoff of the lens can be less attenuated. High-contrast processes which operate near the lens cutoff can actually benefit from the obstruction.

C. Condenser optics

The requirements on condenser optics pose some unresolved tradeoffs between image resolution and depth of field. Although these tradeoffs have been treated carefully for lamp illumination,⁶ the partial spatial and temporal coherence of excimer laser radiation leads to a more complex situation for which no complete analysis has yet been made.

In the experiments described here, the output divergence of the excimer laser (operating at 193 nm) was 1×6 mrad. Direct input without condenser optics would fill a small fraction of the collection cone in the Schwarzschild objective, degrading resolution. A simple diverging lens, as indicated in Fig. 1, can fill the collection cone, although the spatial incoherence of the illumination is not increased. Two methods have been explored as means to increase the spatial incoherency and uniformity by multiplying and randomizing the spatial modes contributing to the mask illumination. Although of limited importance for the $36\times$ system, these increases will be particularly significant in obtaining optimum performance with practical projection objectives which are likely to operate at lower demagnifications and, therefore, with larger collection cones.

The first approach, explored briefly, was to increase the number of contributing modes within the laser cavity by using as a rear mirror aluminum deposited on a roughened quartz blank. With this mirror, the ArF discharge operates with reduced spatial coherence in a condition of amplified spontaneous emission. The number of spatial modes contributing to the output is increased without the full sacrifice in power that occurs using the discharge as a simple flash lamp. The intensity uniformity and, importantly, the long-term stability of the ArF output is also improved. Although promising for multipulse conventional-resist exposure, this approach was found to be too lossy for systems requiring higher peak powers.

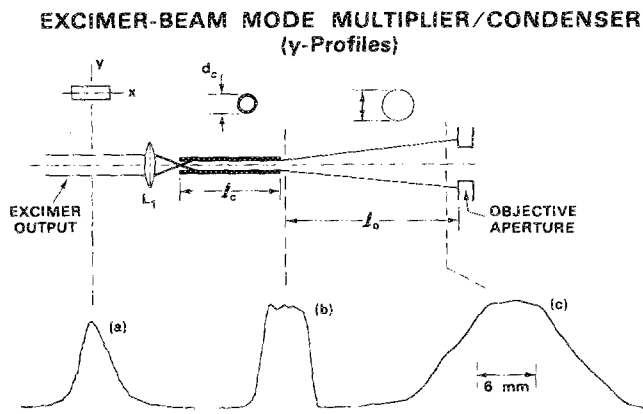


FIG. 2. Hollow waveguide condenser for reduction of coherency in excimer projection. The input optical-intensity profile (a) and resulting near-field (b) and far-field (c) output profiles for a 6-mm-i.d. by 140-mm-long guide filled by light focused with a 38-mm-focal-length lens are shown.

The second approach, used in the experiments below, made use of a hollow tube operated as a diffusing waveguide. Similar methods based on solid glass rods,⁷ multiple prisms,⁸ or mirrors⁹ have been proposed for increasing the intensity uniformity of the excimer output. A hollow 6-mm-i.d. quartz waveguide, with good transmission at 157 nm, was overfilled using a simple single-element lens in the geometry of Fig. 2. The input light is scattered between spatial modes as it is reflected at grazing incidence along the length of the guide. As well as increasing the intensity uniformity, the spatial incoherency and divergence are increased. The resulting near- and far-field intensity patterns for the output from a 140-mm-long 6-mm-i.d. guide are shown in Fig. 2.

III. MATERIAL SYSTEMS

A. Organic layers

Jain *et al.*³ have pointed out the potential advantages of excimer sources for expose-and-develop deep-UV lithography. Possible increases in sensitivity and contrast, however, have not yet been exploited. Although recent experiments have suggested that doses may be reduced using pulsed high-fluence exposure¹⁰ for the inorganic GeSe_x system, multipulse exposure of several Shipley (AZ) organic systems at fluxes $< 5 \text{ MW/cm}^2$, has neither decreased nor

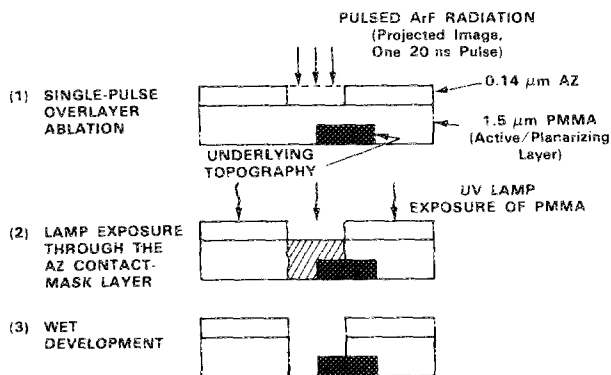


FIG. 3. Procedure for patterning an organic bilayer by single-pulse excimer projection (see text).

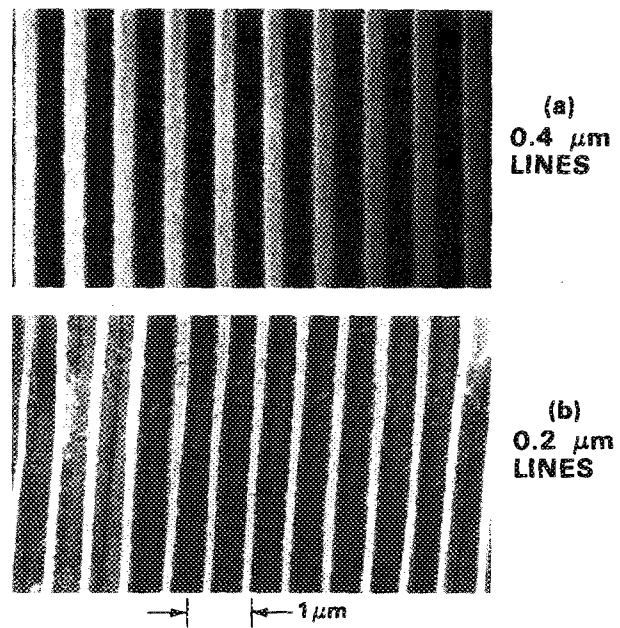


FIG. 4. (a) Scanning electron micrograph of 0.4- μm lines and spaces produced by 193-nm-induced photoreaction of an organic bilayer. The structure shown is in a 1.5- μm -thick PMMA layer (single-pulse exposure). Similar results are obtained with 157-nm radiation. (b) Scanning electron micrograph, similar to Fig. 4(a), of nominal 0.2- μm lines in a 1.5- μm -thick PMMA. Some damage is done to the fragile structure in the process of the electron microscopy.

increased¹¹ quantum efficiencies. For single-pulse exposure, several experiments¹² have demonstrated an increase in efficiency of PMMA exposure at fluences exceeding 2 MW/cm^2 . However, our experiments suggest that, on absorbing substrates such as Si, this occurs only at instantaneous radiation levels near those causing uncontrolled ablation of the resist. Although more feasible in contact-printing geometries^{4,12} or with very thin resist layers, good resolution could not be achieved at these high fluences in optical projection.

In order to maintain high resolution at high dose rates, we have studied systems very similar to previously studied organic bilayers^{13,14} and find that the advantages cited in the early work with lamps and additional advantages apply with excimer projection. A modified method of use, in which the top layer is reactively decomposed by 157- or 193-nm irradiation, has permitted single-pulse printing of 0.4- μm lines and spaces. The procedure is outlined in Fig. 3. The bilayer is formed by overcoating a 1.5- μm -thick soft-baked polymethylmethacrylate (PMMA) layer with several UV absorption lengths of AZ 1350J resist. The top layer can be removed by ablation with a single pulse without disrupting the underlying PMMA. The image is then developed using UV flood exposure and wet etching in isopropanol/MIK.

A primary advantage of the bilayer is that thin AZ-resist imaging layers can be used. Importantly, a thin contamination or remnant of this layer left after ablation does not ultimately interfere with clean development to the substrate surface. Nominal 0.4- μm lines and spaces in 1.5- μm -thick PMMA are shown in Fig. 4. A partially successful attempt to produce 0.2- μm lines on 0.8- μm centers is shown in Fig. 5. Both were produced using single pulses of 193-nm radiation; comparable results, but without significant improvement

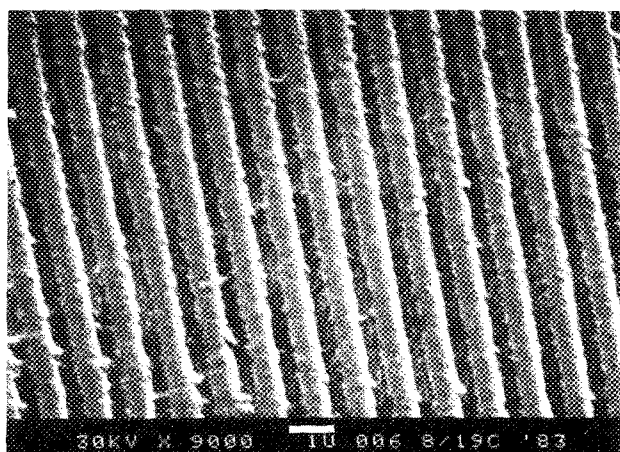


FIG. 5. Scanning electron micrograph of nominal $0.4\text{-}\mu\text{m}$ lines and spaces produced by 193-nm-induced direct etching in an optical-projection geometry three 20-ns pulses, 200-Torr H_2 .

within our limited optimization, were observed with 157-nm radiation. The highly nonlinear intensity response of the overlayer to ablation produces high resolution and sharply defined edges. The required single-pulse fluence is $\sim 80\text{ mJ/cm}^2$, at 193 nm.

B. Laser doping

Recently, the generation of doping defects in Si by laser chemistry was developed as a technique for area (unpatterned) formation of $p\text{-}n$ junctions.¹⁵ This same process has been proposed (and demonstrated at large feature sizes) as a key step in complete laser fabrication of bipolar devices in Si.¹⁶ Such patterned doped films may also be useful, in conjunction with preferential etches, as an inorganic-resist masking material for subsequent lithography. An attempt was made, in our experiments, to extend this process to submicrometer projection patterning.

The mechanism involves combined photochemical/thermal generation of free dopant atoms, in the present experiments free B from 30 Torr of BCl_3 vapor, followed by rapid diffusion in a several-hundred-nanometer-thick liquefied Si layer.^{15,16} The latter is formed by the same excimer-laser irradiation which liberates the dopant. The dominant source of dopant atoms is by the photochemical or thermal cracking of adsorbed BCl_3 . Efficient incorporation of several adsorbed monolayers is sufficient to dope a thin Si layer to solid solubility ($\sim 6 \times 10^{20}/\text{cm}^3$). Ultimately, the resolution of the process is limited to lateral heat-diffusion lengths, which, at these temperatures, for Si, are $\sim 100\text{--}200\text{ nm}$. Consistent with this, $< 0.5\text{-}\mu\text{m}$ features (as confirmed by secondary electron emission differences) have been achieved.

C. Etching of glass

Laser-induced reactions at surfaces in contact with adsorbed and vapor phases have been used widely in focused-beam (direct-writing) geometries for maskless deposition and etching.^{2,3} Many reactions are characterized by high

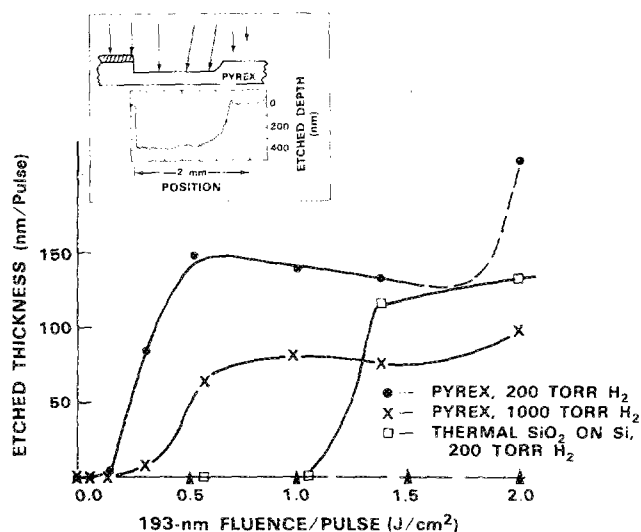


FIG. 6. Etched thickness for Pyrex and 650-nm-thick thermally grown SiO_2 on Si as a function of pulse fluence for ArF-laser irradiation under 1000 and 200 Torr of H_2 . The inset shows a depth profile after 3-pulse exposure at 0.8 J/cm^2 (200 Torr H_2).

contrast, e.g., $\gamma = 20\text{--}50$, and, consequently, are capable of high resolution and of accurate patterning with low optical modulation depth.¹⁷ Many of these processes can be adapted to excimer projection patterning. Patterning processes relying on heating alone can have flux requirements in the range of several hundred mJ/cm^2 , not too different from optimized photoresists in the visible.

Initial experiments have been completed in a system in which etching of silica glasses in H_2 vapor is promoted by transient heating. Most of the exposures were carried out on Pyrex substrates using 193-nm irradiation; an example is shown in Fig. 5. Transient laser heating to the glass softening temperature rapidly erodes the surface in areas confined to the projected image. The fluence dependence of the rate is shown in Fig. 6. A relatively sharp threshold for etching near 200 mJ/cm^2 is consistent with strong heating accompanied by possible nonlinear absorption processes. At slightly higher fluences, $\sim 400\text{ mJ/cm}^2$, Na D-line emission is visible in the vapor phase above the surface. The rates in this regime are too large to be explained by collisions between H_2 vapor and the surface, and therefore are likely to include important effects from physical or optical ablation.¹⁸ Note that a reduction from 1000 to 200 Torr of H_2 actually causes an increase in net rate. Further reduction to < 100 Torr causes a slight further increase, but also an obvious increase in particulate roughness. A stylus trace showing the etch uniformity of a shadowed etch pit resulting from three 193-nm pulses at near optimum conditions is shown in the inset.

Unlike with direct projection etching of comparably thick organic films, with this system high-resolution imaging was found possible. A typical result for nominal $0.4\text{-}\mu\text{m}$ lines and spaces is shown in Fig. 6. Rates of $10\text{--}20\text{ nm/pulse}$ are possible at a 200-Torr H_2 pressure while maintaining submicrometer resolution. Edges on deeply etched structures show a relatively large, 100-nm-scale edge roughness (compare Fig. 5 to Fig. 4).

D. Solid-state chemistry: Al/O

In principle, a variety of transformations can be induced by laser irradiation of metastable solid films. Here, we describe a solid-state transformation system based on evaporated Al/O cermet.¹⁷ This system and other metal/dielectric composites are particularly interesting since both chemical (e.g., etch resistance) and electrical properties can be altered with a heat pulse, and since they are immediately compatible with subsequent high-temperature processing.

In our studies, a 30-nm-thick Al/O cermet was deposited on oxidized Si wafers by Al evaporation under an O₂ ambient. Best results were with room-temperature evaporations at $2\text{--}5 \times 10^{-6}$ Torr O₂ pressures. As evaporated, these films have a sheet resistance of $1000 \Omega/\square$, and are smooth and shiny in appearance. The conversion process in these films was correlated with visible color changes by measurement of reflectance changes at 632.8 nm. The power dependence of the transformation is shown in Fig. 7, after low-power single-pulse excimer laser irradiation, the films turn black; after higher-power irradiation the films are silvery. These color changes correspond to the creation of new phases with markedly different chemical-etching properties and electrical conductivities, e.g., the black phase has a sheet resistance of $> 10^6 \Omega/\square$. A second curve shows the induced reflectance for a cumulative 100-pulse exposure. Note that a silver phase is not formed; the irreversible transformation to the complete black phase occurs at $\approx 1/10$ of the peak fluence required using single pulses.

The conductivity change induced by excimer pulses is of potential use for defining conductor patterns without any further treatment. Alternatively, the transformed material can be used as an etch mask to pattern underlying materials. To demonstrate the second application, images were transferred into SiO₂ by wet etching in nitric-acid/phosphoric-acid followed by reactive-ion etching in CH₃F. Typical results obtained with single-pulse excimer-laser exposure are shown in Fig. 8. The projected image shows edges defined to a small fraction of a micrometer.

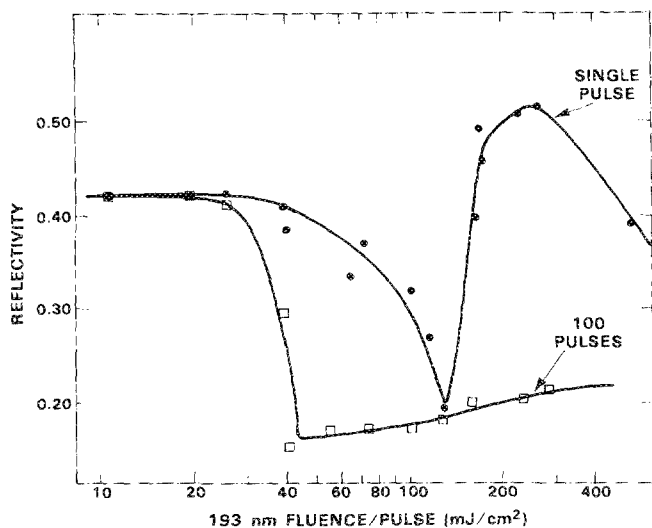


FIG. 7. 632.8-nm reflectances of 30-nm-thick Al/O cermet films, following 193-nm pulsed irradiation, as a function of pulse fluence. The reflectance is correlated with visible color changes.

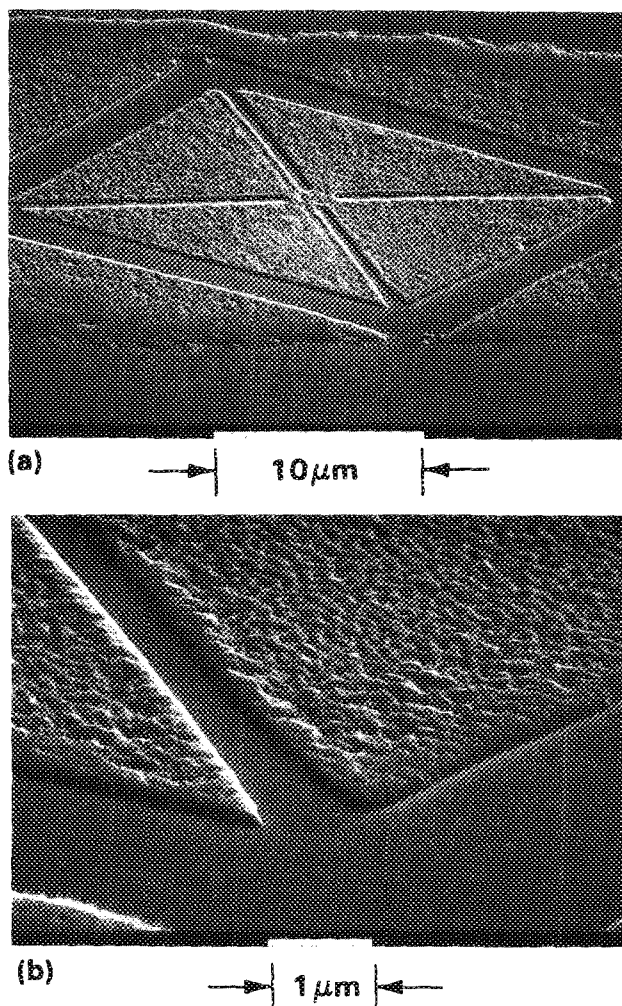


FIG. 8. Thermally grown SiO₂ patterned by single-pulse transformation of an Al/O cermet. The 30-nm-thick transformed cermet is used to mask dry etching (see text).

To elucidate the nature of the transformation, Auger depth profiling was performed. As shown in Fig. 9, the as-deposited film is a mixture of Al and Al₂O₃. The metal is distinguished in the Auger spectrum from the oxide by a slight shift in the low-energy aluminum peak near 50 eV. After laser irradiation and transformation into the black film, the Al₂O₃ phase becomes more pronounced near the surface, suggesting the growth of chemically resistant Al₂O₃ from the surface inwards. This growth may be nucleated by the native surface oxide. Deeper within the film, the composition shifts toward Al. Transmission-electron-microscope studies show an increased grain size in the black phase. At higher energies, in the silver phase, the Al₂O₃ is more pronounced in the interior of the film. One possibility is that at these higher pulse energies the film melts; as the film solidifies, the thermodynamically more stable phase, Al₂O₃, freezes out first, and there is no compositional grading. This is consistent with the sharpness of the onset of the silver phase as the fluence is increased in Fig. 7.

IV. DISCUSSION

In the section above we have outlined exploratory studies of excimer-laser projection imaging using material systems

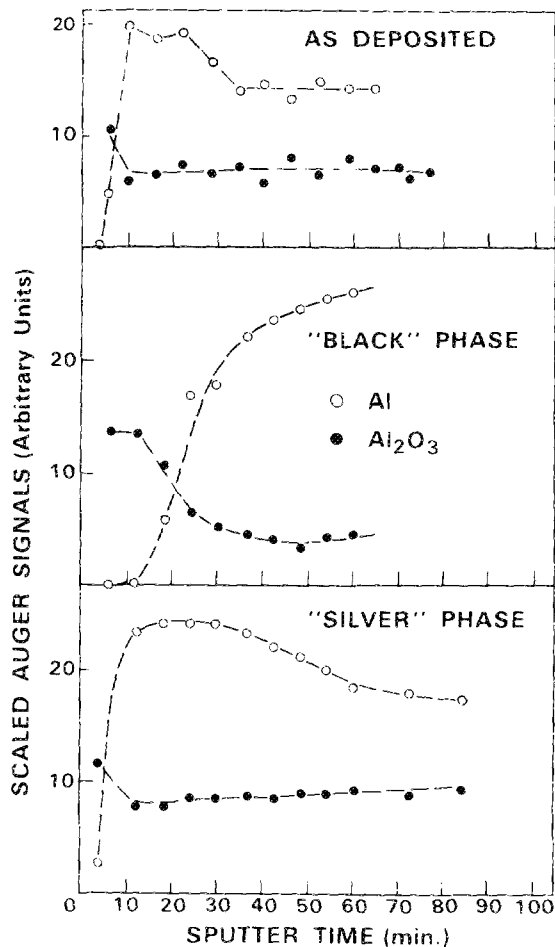


FIG. 9. Composition as a function of depth of ArF-laser irradiated Al/O films as determined by Auger depth profiling. Films are identified according to the color changes of Fig. 7.

which, for practical reasons, are not suitable for conventional lithography with lamp sources. The high efficiency and pulsed nature of the excimer output, moreover, alter the criteria for evaluating such systems. The primary findings of these characterizations are shown for comparative purposes in Fig. 10. There are three broad categories of material systems.

The most sensitive systems at the low dose rates characteristic of lamp (or low-intensity excimer) irradiation are injected-defect systems. Such systems are optimized for radiation sensitivity by exploiting the overall gain in quantum yield that can be produced in subsequent dissolution or etching rates, due to low densities of induced defects. This approach has been uniquely successful with low-intensity lamp sources and is unquestionably the method of choice (when multiple-step processing is acceptable) for excimer irradiation at very low ($< 10 \text{ mJ/cm}^2$ pulse) dose rates. The AZ-1450J, PMMA and GeSe_2 (at $< 5 \text{ mJ/cm}^2$ pulse) systems are examples of such materials; as demonstrated by others, all can operate successfully with excimers, although the most sensitive Novalak-based materials, such as AZ-1450J, are restricted to the longer excimer wavelengths.

A second category of systems is designed around direct interfacial chemistry with an external vapor or liquid. This includes the majority of laser-photochemical and laser-ther-

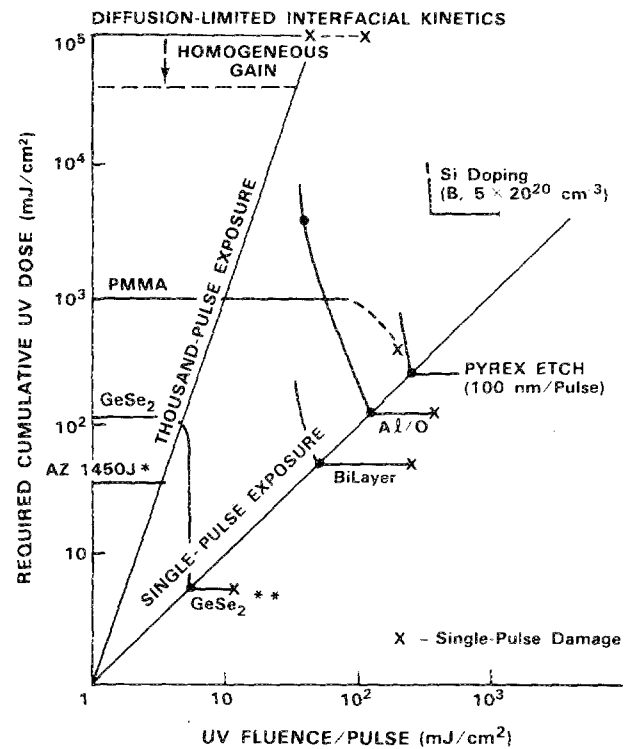


FIG. 10. Integrated total UV dose requirements as a function of pulse fluence for excimer-laser patterning. Material systems are divided in the text into (1) injected-defect materials (AZ-1450J, GeSe_2 , PMMA, and Si doping), (2) direct interfacial chemical systems (hypothetical, e.g., photodeposition), and (3) nonlinear transformation materials (Al/O, bilayer, Pyrex etching, GeSe_2). Response characteristics, once single-pulse exposure has been achieved, are drawn as horizontal lines to higher fluence, since fractional-pulse exposure is impractical. X indicates visible damage.

mal deposition, as well as laser-photochemical etching, methods. Such processes are limited fundamentally by the material coverage of an adsorbate, or by surface-collision frequencies from the external phase. For the case of substrate/adsorbate reactions at modest ($> 10 \text{ mTorr}$) pressures, the adsorbate coverage can be assumed to have reached equilibrium in between laser pulses. The maximum reacted thickness per pulse is then approximately equal to the adlayer thickness itself. The actual reacted thickness per pulse may be less, depending on the process. As an example, with the assumption of a relatively large UV cross section of 10^{-17} cm^2 , Fig. 10 shows the characteristic for an interfacial deposition or etching reaction requiring layer-by-layer photochemical reaction of $\sim 10^3$ monolayers of an adsorbate, for a total reacted thickness of several hundred nanometers. Moreover, because of the onset of physical ablation, most photodeposition reactions cannot operate well at high pulsed fluences. For the case of substrate/gas-phase reactions at subatmospheric pressures, the reacted thickness per pulse is limited to the gas exposure per pulse. For 8–20 ns pulsewidths, this is approximately 1 langmuir.

As a result of these limitations on reacted thickness per pulse, the low duty factor ($\sim 10^{-5}$) of current excimer lasers implies long exposure times. We note that these rate considerations, applicable to patterned photodeposition, are not

encountered in the geometry of unpatterned large-area deposition, in which photolysis is homogeneous in the volume adjacent to the substrate. One possible method of reducing the dose requirements is to use the laser reaction as a surface-preparatory step, such as prenucleation, in combination with gain from homogeneous reactions, as is done routinely with direct-write photodeposition.² A second possible method, the only one explored here, is to use interfacial chemical systems that can take advantage of gain from defect injection. The B doping reaction for Si in combination with differential etching can be thought of as such a case; note (see Fig. 10) that the dose requirement is in fact reduced relative to the hypothetical pure-interfacial-chemistry case. It should also be emphasized that for some applications the advantages of single-step processing may compensate for the high dose requirements of interfacial chemistry.

A third category of systems is nonlinear homogeneous transformations, in which laser radiation drives a reaction or phase change within a thin film. These include the majority of the systems examined in this study (Al/O, bilayer and glass etching) and are the only systems showing good single-pulse imaging. All make explicit use of the higher dose rate possible with excimer lasers relative to lamps. The GeSe₂ inorganic exposed with pulses of >5 mJ/cm² fluences should also be considered in this class.¹⁰ It is notable that the dose requirements for favorable systems in this category can be comparable to those of highly optimized injected-defect photoresists. All of the systems studied make more efficient use of deep UV photons than can be obtained by exposure of PMMA.

V. CONCLUSION

In this initial study, we have attempted to identify reactive material systems which take explicit advantage of the pulsed nature and short (193 and 157 nm) wavelengths of excimer laser sources for submicrometer patterning. The immediate application for these systems would most probably be with projection aligners in a reduction step-and-repeat configuration, since this arrangement allows full use of the transient high peak power from these sources.

The systems studied are classified as injected-defect, interfacial-chemical, and solid-transformation materials. Although the first category includes systems with lower demonstrated dose requirements at low dose rates, e.g., with lamps, it is argued that intrinsically high-dose-rate solid-transformation systems may be preferred for excimer projection imaging. This is largely because of the potential to optimize processing properties, such as etch resistance and high-temperature durability, which have historically been accepted in a less optimized state in lamp photoresists. The class of interfacial-chemical systems, which includes many deposition and etching processes developed for laser direct writing, has higher integrated-dose requirements because of limitations on material transport during short pulses. The development of higher repetition-frequency excimer lasers would help in the implementation of these processes.

Among the systems studied, the most promising results have been obtained with an organic bilayer and an inorganic Al/O cermet film. With available laboratory optics, we have

demonstrated projection printing in these systems at feature sizes of ~ 0.4 μm . Marginally resolved 0.2- μm lines have been obtained in the bilayer. Such results are notable in that, in spite of the imperfect optics, they are within a factor of ~ 2 of the MTF "cutoff" dimension, $\lambda/2\text{NA}$, for diffraction-limited optics at the numerical aperture of the system. This high resolution with aberrated optics is possible because of the high effective contrast that can be obtained using pulsed laser radiation relative to lamp exposure of photoresists.¹⁶ Further developments of such high-contrast systems could relax the design requirements for excimer-laser projection aligners, and with higher-numerical-aperture optics, could permit higher resolution than is now possible in resists optimized for lamp exposure. The tradeoff, with increasing contrast, between resolution and increased requirements on dose control has been analyzed previously,¹⁶ and has been shown to optimize, according to simplest first considerations, at $\gamma \sim 5-10$. This is close to the contrast of several of the reactive systems studied. Higher-than-optimum γ is found in several other cases; however, this parameter is likely to be adjustable, in most systems, by varying the external parameters of temperature and gas pressure.

The dose required for the new systems ranges from 40-300 mJ/cm², depending on the radiation-induced reaction, and on the optical and thermal properties of the irradiated surface. This compares favorably with the sensitivity of highly optimized conventional deep-UV resists. A specific attempt has been made to demonstrate patterning by single pulses in the new systems.

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¹See, for example, K. Emery, P. K. Boyer, L. R. Thompson, R. Solanki, H. Zarnani, and G. J. Collins, in *Proceedings of the SPIE Conference on Laser-Assisted Deposition, Etching and Doping* (Los Angeles, California, 1984), Vol. 459, and references therein.

²For recent reviews, see D. J. Ehrlich and J. Y. Tsao, in *VLSI Electronics: Microstructure Science*, edited by N. G. Einspruch (Academic, New York, 1984), Vol. 7, pp. 129-163; D. J. Ehrlich and J. Y. Tsao, *J. Vac. Sci. Technol. B* 1, 696 (1983).

³G. M. Dubroeuq and D. Zahorsky, *Proceedings of the International Conference on Engineering* (1982), p. 73; K. Jain, C. G. Willson, and B. J. Lin, *IBM J. Res. Dev.* 26, 151 (1982).

⁴Resist ablation in a contact-printing geometry was first demonstrated by R. Srinivasan and V. Mayne-Banton, *Appl. Phys. Lett.* 41, 576 (1982).

⁵M. Brady and A. Davidson, *Rev. Sci. Instrum.* 54, 1292 (1983).

⁶The spatial-coherence considerations for lamp condensers are treated in A. C. Liu and B. J. Lin, *IEEE Trans. Electron Devices* ED-30, 1251 (1983).

⁷P. H. Bucksbaum and J. Bokor, in *Excimer Lasers-1983*, AIP Conference Proceedings No. 100, edited by C. K. Rhodes, H. Egger, and H. Pummer (American Institute of Physics, New York, 1983), p. 279.

- ⁸Y. Kawamura, Y. Itagaki, K. Toyoua, and S. Namba, *ibid.*, p. 288.
- ⁹K. Jain, *Lasers and Applications* (1983), p. 49.
- ¹⁰K. J. Polasko, D. J. Ehrlich, J. Y. Tsao, R. F. W. Pease, and E. E. Marinero, *IEEE Electron Dev. Lett.* EDL-5, 24 (1984).
- ¹¹S. Rice and K. Jain, *IEEE Trans. Electron Devices* ED-31, 1 (1984).
- ¹²Y. Kawamura, K. Toyoda, and S. Namba, *App. Phys. Lett.* 40, 374 (1982); J. C. White, etc., a similar increased sensitivity has been observed with pulsed exposure of x-ray resists, B. Yaakobi, H. Kim, and J. M. Soares, H. W. Deckman and J. Dunsmuir, *App. Phys. Letter.* 43, 686 (1983).
- ¹³B. J. Lin, in *Fine Line Lithography*, edited by R. Newman (North-Holland, Amsterdam, 1980), pp. 105-233.
- ¹⁴N. N. Efremow, Jr. (private communication).
- ¹⁵T. F. Deutsch, J. C. C. Fan, G. W. Turner, R. L. Chapman, D. J. Ehrlich, and R. M. Osgood, Jr., *App. Phys. Lett.* 38, 144 (1981).
- ¹⁶K. G. Ibbs and M. L. Lloyd, in *Laser-Chemical Processing of Surfaces*, edited by A. W. Johnson, D. J. Ehrlich, and H. R. Schlossberg (Elsevier, New York, 1984).
- ¹⁷D. J. Ehrlich and J. Y. Tsao, *App. Phys. Lett.* 44, 267 (1984). Some of the physical properties of Al/O cermets are described in H. Gurev, *Thin Solid Films* 18, 275 (1973).
- ¹⁸V. Daneu, J. Peers, and A. Sanchez, in *Laser-Chemical Processing of Surfaces*, edited by A. W. Johnson, D. J. Ehrlich, and H. R. Schlossberg (Elsevier, New York, 1984).