Extended Abstracts of the 15th Conference on Solid State Devices and Materials, Tokyo, 1983, pp. 109-115

Invited

Microelectronic Thin Film Deposition by UV Laser Photolysis

P. K. Boyer, C. A. Moore, R. Solanki, W. K. Ritchie and G. J. Collins

Department of Electrical Engineering
Colorado State University
Fort Collins, CO 80523

An excimer laser is used to photochemically deposit thin films of silicon dioxide, silicon nitride, and aluminum oxide, at low temperatures (100-450°C). High deposition rates and conformal step coverage were demonstrated. The films exhibit low defect density and high breakdown voltage and have been characterized using IR spectrophotometry, AES, and C-V analysis. Additionally, we have deposited metallic films of Al, Mo, W, and Cr at room temperature over large (>5 cm^2) areas.

Introduction

There exists a need for low-temperature semiconductor fabrication processes to minimize wafer warpage, dopant redistribution, and defect generation and propagation.[1] Moreover, film deposition over photoresist for applications such as tri-level resists for high-resolution lithography and direct patterning via lift-off is desired at temperatures below ∿200°C (above which resist degradation occurs).[2] In this work we discuss a new low temperature, high deposition rate (up to 2500 Å/min) film growth technique which uses an excimer laser to photolyze gas-phase reactants whose products condense and form the desired film. This technique has been used to deposit dielectric films of SiO_2, Si_xN_y, and Al_2O_3, and conducting films of Al, Cr, Mo, and W. The properties of these films are reviewed and compared to conventional deposition techniques.

Experimental Apparatus

A Lumonics 860T excimer laser provides ultraviolet photons in a beam of rectangular cross section which is down-collimated to a cross-sectional area of 12 x 1.5 mm for parallel deposition, as shown in Figure 1, or is expanded using a negative lens to deposit over large areas during perpendicular irradiation. The insulating films in this work were deposited using a wavelength of 193 nm (ArF* transition) while the metallic films were deposited using either 193 nm or the 248 nm (KrF*) wavelength; repetition rate for each wavelength was 90-100 Hz. UV transmitting windows were purged with a rare gas to prevent deposition on them. Surface reaction photons, whose role is described herein, were provided by folding back the portion of the beam transmitted through the cell. A substrate heater capable of heating up to 500°C was used during the deposition of dielectric films.

A major advantage of this experimental scheme is the ability to vary laser power, wavelength, and spatial location independently while not affecting the deposition process. This is in direct contrast to plasma-enhanced CVD where process parameters are strongly interrelated and one is limited to pressure regimes where a discharge can be started and maintained. The only pressure constraint on the laser CVD technique is that the gases used for a given deposition must be at optically thin concentrations. Thus beam attenuation across a sample is minimized and thickness uniformity is preserved. For example, deposition of SiO_2 is possible at total pressures up to 8 torr since the beam intensity will vary by less than 1% across a 3-inch wafer at this pressure.

Additionally, conformal step coverage is possible by this technique due to the photodissociation volume being an "infinite plane source" with respect to topographical features on the sample.

Deposition of Oxide and Nitride Films

Films of SiO_2, Si_xN_y, and Al_2O_3 have been deposited via the following reactions, respectively:

$$SiH_4 + N_2O + h\nu(193\ nm) \rightarrow SiO_2 + products \quad (1)$$

$$SiH_3 + NH_3 + h\nu(193\ nm) \rightarrow Si_xN_y + products \quad (2)$$

$$Al(CH_3)_3 + N_2O + h\nu(193\ nm) \rightarrow Al_2O_3 + products \quad (3)$$

The silicon-based insulator films are compared to the other low-temperature deposition schemes of plasma-enhanced and mercury photosensitized CVD, while the aluminum oxide films are discussed on the basis of their properties alone.

Typical deposition conditions for deposition of SiO_2 are shown in Table 1a. A relatively high reactant gas ratio N_2O/SiH_4 was used in this work. Deposition rates (which are for films of area $\sim$20 cm^2) could be increased using a higher silane density since this reactant is optically transparent at 193 nm.

The electrical, chemical and physical properties of the laser CVD SiO_2 films have been measured. The films are comparable to plasma and photo-sensitized CVD films with respect to adhesion, stress, index of refraction, stoichiometry, and hydrogen incorporation as shown in Table 2. Bonded hydrogen in SiO_2 films as a function of substrate temperature, measured by IR transmission spectroscopy (integrated baseline technique), is shown in Figure 2a. As temperature increases, H_2O and SiOH bonded hydrogen is converted to SiH groups in agreement with previous PECVD studies.[3] Figure 2b shows SiO_2 etch rate in 7:1 BHF vs. deposition temperature, and effect on refractive index at 6328 Å. Low temperature films show indication of density reduction (reduced index and increased etch rate). Etch rates at 425°C are significantly less than LPCVD and APCVD SiO_2 films deposited at similar temperatures. Auger results show that laser photo CVD films are not Si rich and have a stoichiometry constant with temperature, for 200-500°C deposition temperatures (Figure 2c). Perpendicular irradiation during growth of SiO_2 films caused significant reductions of hydrogen incorporation, as H_2O, SiOH, and SiH as shown in Figures 3a,b. SiOH absorption at 960 cm-1 and SiH at 880 cm-1 were eliminated. Less drastic reduction of OH groups at 365 cm-1 and H_2O at 3300-3400 cm-1 was also seen due to surface photon irradiation. Effects of increasing SiH_4 flow (an equivalently partial pressure on SiH_4/N_2O ratio) were studied.

Above N_2O/SiH_4 ratios of 35/1, deposition rate increased linearly with SiH_4 flow and stoichiometry and refractive index were constant. For higher SiH_4 flows (N_2O/SiH_4 <35/1) deposition rate increased sublinearly, index of refraction increased sublinearly, index of refraction increased weakly, and measured stoichiometry was essentially constant. Lack of strong effect on film properties from increased silane flow is due to weak photoabsorption by SiH_4 (as compared to N_2O). The laser deposited films are inferior compared to plasma-enhanced CVD films in terms of electrical resistivity, dielectric strength, and etch rate in a buffered oxide etch. Laser CVD films exhibited the lowest internal stress and pinhole densities. A 1000 Å SiO_2 film photodeposited at 400°C had no pinholes in 5 cm^2, while a 2000 Å plasma CVD film showed <1/cm^2 and a 4000 Å photox SiO_2 film had 1 to 5 per square centimeter. In the laser CVD approach conformal step coverage is achieved over a wide range of deposition conditions. Figure 4 shows SiO_2 ($\sim$6500 Å thick) photodeposited over a 4000 Å polysilicon step which was patterned over an oxidized silicon wafer which has been reported elsewhere.[4] It should be noted the rough surface atop the step is due to the underlying poly-Si while the even morphology of the oxide is retained below the step, over smooth oxidized Si wafer.

Silicon nitride has also been deposited using laser-induced CVD using the reaction in equation (2). The conditions for deposition are similar to the two techniques under comparison and to those of the SiO_2 deposition process discussed above (Table 1b). A notable difference is that a lower concentration of ammonia is required since its absorption cross section is $\sim 10^3$ higher than nitrous oxide at 193 nm.[5] Deposition rate is still much higher than that of plasma or mercury sensitized reactions.

Again the photodeposited films have comparable physical properties (i.e., adhesion, compressive stress, refractive index, step coverage and stoichiometry) as shown in Table 3. Pinhole densities are comparable to plasma CVD films but superior to

photride films. The laser CVD films lack in terms of etch rates; they etch approximately ten times faster than plasma deposited nitrides. However, at the bottom of Table 3 the effect of low-level surface irradiation can be seen. As deposited at 380°C, the laser CVD silicon nitride films etched at 44 Å/sec in 5:1 buffered oxide etch, indicative of a porous or low density film. The etch rate was reduced to 8 Å/sec by folding back the transmitted portion of the 193 nm dissociating laser beam. The power density on the substrate surface was weak so as to not cause an increase in steady-state temperature. Clearly, a surface reaction is occurring but has not been modeled at this time. Refer to Figure 1 for surface photon irradiation geometry.

Using this technique, aluminum oxide films were deposited but are not as fully characterized at this time. Conditions for Al_2O_3 growth are tabulated in Table 1c. As compared to films obtained by RF plasma deposition, the laser CVD Al_2O_3 films show comparable adhesion, stress, stoichiometry, and refractive index. As with the silicon compounds discussed previously, the photodeposited films show higher etch rate (x 10) but have a low pinhole density (none in 5 cm^2 for an 1100 Å laser CVD film versus 36/cm^2 for a 2500 Å plasma deposited film). The only other major difference known presently is that the photodeposited films have shown up to 1% carbon contamination, probably due to dissociation of methyls in the aluminum donor gas. The effect of this impurity on the electrical properties is not known at this time.

Deposition of Metals

We have previously reported laser-induced deposition of refractory metals over small areas (10^{-4} cm^2).[6] As an extension of our earlier work we have investigated large area (>5 cm^2) photodeposition of Al, Mo, W and Cr. Uniform films of these metals were deposited on pyrex and quartz substrates as well as silicon wafers at room temperature. We have examined the resistivity, adhesion, stress, and step coverage of these films.

Plasma assisted CVD of refractory metals occurs as low as 350°C (nm/min deposition rates) for refractory halides[7] but plasma parameters such as rf power and frequency, gas flow, electrode spacing, total pressure and substrate heating are all interrelated and difficult to control individually. Photodissociation occurs only along the path of the laser beam, unlike plasma excitation, therefore there is less impurity generation from the walls due to plasma ion bombardment. Moreover the cracking pattern is less complex in photodissociation and hence we have better control and repeatability of deposition conditions.

Our experimental arrangement is shown in Figure 1. All substrates were precleaned in HF and deionized water prior to deposition. The substrates were held either parallel or normal to the incident laser beam. Either a reservoir containing the carbonyl or a flask of trimethylaluminum (TMA) was connected to the cell. For the carbonyls, both the reservoir and the pyrex connecting tube were heated with a heater tape to 50°C.

The substrate was first placed into its holder and the cell pumped down with a roughing pump to a few microns. The laser then irradiated the substrate to preclean the surface with the UV radiation; this improves the adhesion of the deposited films. The vacuum pump was then throttled to reduce the cell throughput and the donor gas introduced into the cell. The deposited films appeared as bright silvery films. When the beam was parallel to the substrate, black particulate films of columnar growth resulted, as shown in Figure 3. For this reason, all the films characterized were obtained at normal incidence. Thick (>1 μ) Cr and Mo films deposited at room temperature had a tendency to peel when exposed to air. This could be avoided by heating the substrate to about 150°C during deposition or prior to removal from the cell. All the photodeposited films discussed below were obtained at room temperature.

The purity of photodeposited films was examined by Auger and ESCA analysis. The major impurity in all the films was oxygen (<7%) probably due to the relatively poor vacuum obtained with a roughing pump. We hope to reduce this impurity by using an improved deposition cell and a better vacuum system. An attractive result was the relatively low concentration of carbon in these films (Table 4). The most carbon-free films and the highest deposition rates were obtained using a laser wavelength of 248 nm. But even this low contamination by

carbon can limit the obtainable film resistivity.[8] These rates will vary with the laser power, the cell pressure, and the size of the area over which the film is deposited. The film over the 2.5 x 2.5 cm area was uniform to ±15%. It should be pointed out that the area of deposition can be varied by changing the divergence of the laser beam with a lens; with tight focusing and substrate or beam translation, patterned lines can be deposited.

The adhesion of the photodeposited films was measured. In the case of W, the machine reached its upper limit without detaching the films, while in the case of Al, Mo and Cr, the quartz substrates chipped off before the films were detached. The most adhesive films were deposited using the 193 nm laser wavelength for photodissociation. Stress measurements of the photodeposited films were made by the substrate bending technique on microscope cover slips. All the films had tensile stress and none was higher than 7×10^9 dynes/cm^2; aluminum showed the lowest amount of stress (1×10^9 dynes/cm^2).

The electrical resistivities of the deposited metal films were measured with a four-point probe. These resistivities are tabulated along with the bulk values of Table 4. The aluminum had, even with its high carbon content, a resistivity approaching the bulk value. The measured resistivities of the refractory metals were not corrected for thin film effects.

One important quality of a film deposition technique is the ability of the deposited film to cover vertical-walled steps. Step coverage patterns used to check our deposited refractory films were the same as those used to examine SiO_2 step coverage. The photodeposited refractory metal thicknesses were varied between 0.2 and 0.6μ. After deposition, the metal-coated wafers were chilled in liquid nitrogen and then cleaved. The step coverage was examined with a SEM. An ∿5000 Å Al film is shown in Figure 4. It can be seen that the film is of even thickness over the flat, as well as the vertical walls, and clearly demonstrates conformal step coverage. Surface cleaning by transient heating and UV desorption of surface contamination, in combination with uniform flux of photoproducts, contributes to the conformal coverage of and the absence of voids under the metal films as shown in Figure 5. The vertical striations in the films are due to water cleaving. It is interesting to note that SEM examination of all our films showed absence of microstructures similar to those seen in laser photodeposited Cd and Zn films.[9]

Summary

We have described a technique to deposit oxide, nitride, and metal films via ultraviolet photolysis of gas-phase donor molecules. All films are deposited at fast rates and demonstrate conformal step coverage over vertical steps. The insulating films exhibit low pinhole densities but are inferior in terms of etch rate and electrical resistivity. Surface photon impingement during film deposition is shown to reduce silicon nitride etch rate. Metallic films have been deposited and exhibit good physical properties. The refractory metals show high resistivities which may be limited by carbon incorporation. The effect of annealing these films has not been studied yet.

Acknowledgements

The authors would like to acknowledge the Office of Naval Research and ASM America, Inc., for support of this work.

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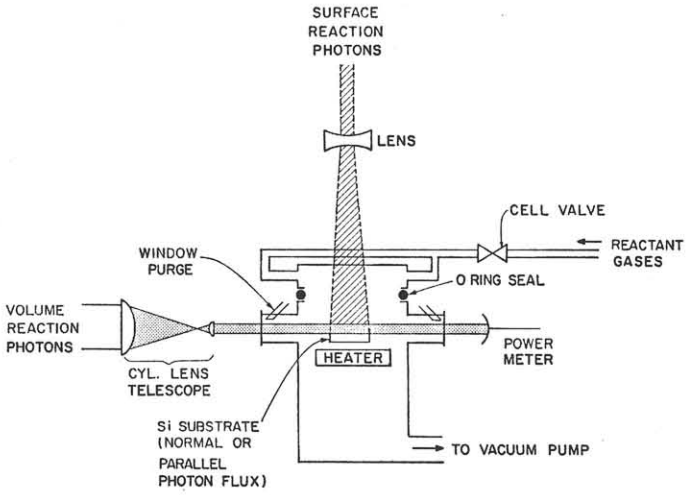

Figure 1. Experimental Set-Up

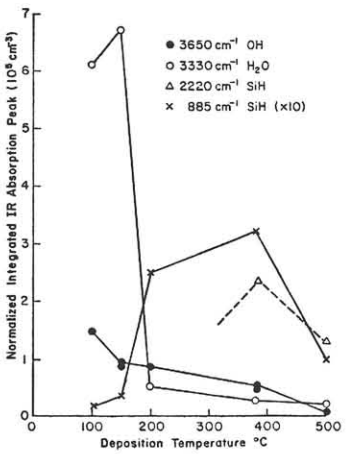

Figure 2a. IR Transmission through SiO_2 Film

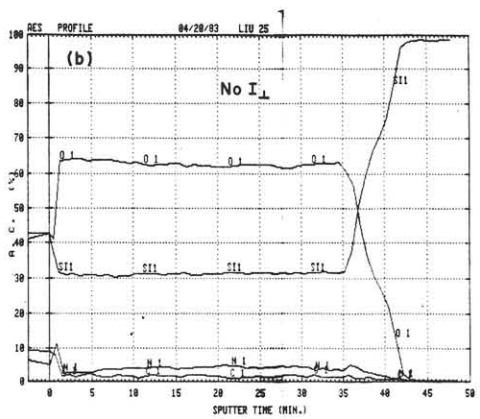

Figure 2c. Sputtered Auger Profile of SiO_2 Film

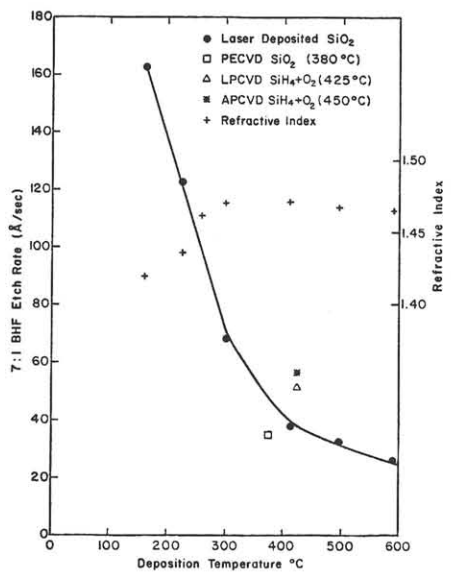

Figure 2b. SiO_2 Etch Rate in Buffered HF

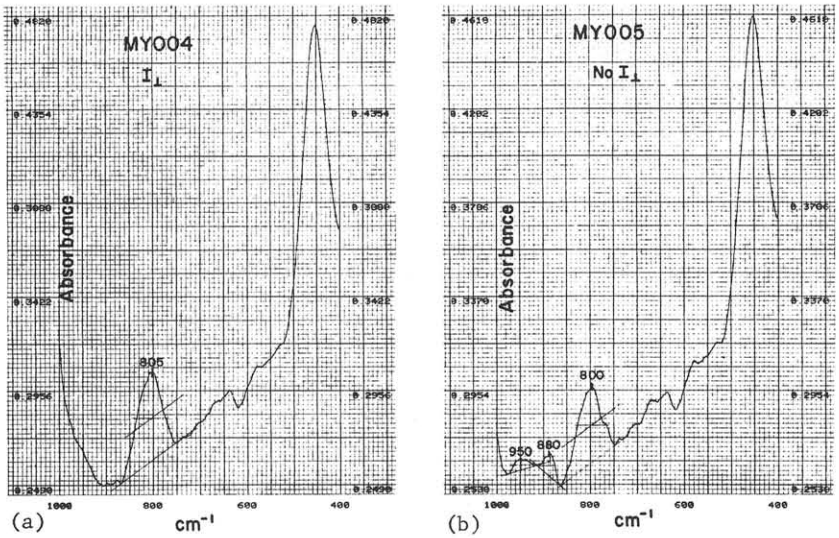

Figure 3. Hydrogen Incorporation (a) with and (b) without Perpendicular Irradiation

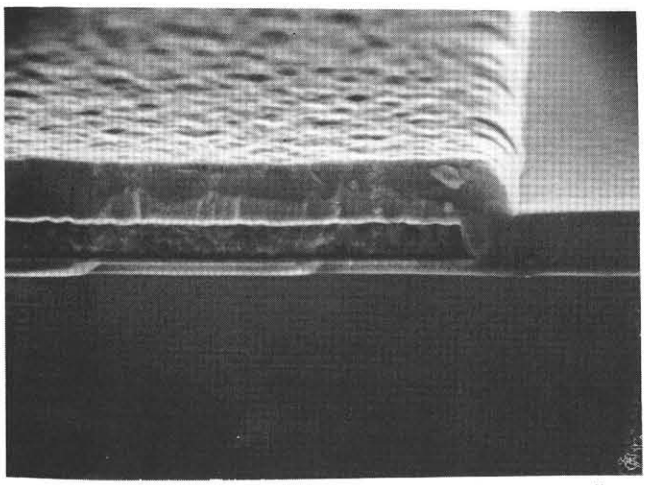

Figure 4. Step Coverage of SiO_2 over 4000 Å Polysilicon Step

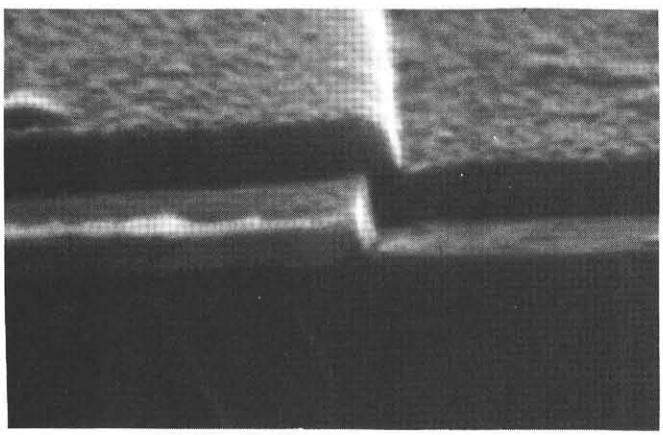

Figure 5. Step Coverage of 5000 Å Aluminum Film over 4000 Å Polysilicon Step

Table 1. Typical Deposition Conditions

a) SiO_2	Laser	RF Plasma[1]	Hg Photox™,[3]
Substrate temperature	150-400°C	380°C	100-200°C
Cell pressure	6 Torr	1.1 Torr	0.3-1 Torr
$N_2O/SiH_4/N_2$	80/1/40	33/1/0	25/1/0
Deposition rate	800 Å/min (N_2 buffer)	300 Å/min	120 Å/min
b) Si_xN_y	Laser	RF Plasma[1]	Hg Photride™,[3]
Substrate temperature	200-425°C	380°C	150-200°C
Cell pressure	2 Torr	2 Torr	4 Torr
$NH_3/SiH_4/N_2$	1/1/40	7/1/0	30/1/0
Deposition rate	700 Å/min	350 Å/min	65 Å/min
c) Al_2O_3	Laser	RF Planar Magnetron[2]	
Substrate temperature	100-400°C	150-400°C	
Cell pressure	1 Torr	10^{-2} Torr	
Deposition rate	1500 Å/min	350 Å/min	

[1]Reactor manufactured by ASM, Phoenix, AZ.
[2]R. S. Nowicki, J. Vac. Sci. Tech. 14(1), 127 (1977).
[3]Tylan Corporation, Solid State Technology, Dec. 1982.

Table 2. Comparison of Deposited SiO_2 Films

	Laser CVD	Plasma	Hg Photox
Breakdown field (MV/cm)	6.5-8 (1000 Å film)	10 (2000 Å)	4-8 (1000-10,000 Å)
Pinhole density (cm^{-2})	1 (1000 Å film)	1 (2000 Å)	1 (4000 Å)
Resistivity (Ω-cm) at 5 MV/cm	up to 6.7×10^{13}	10^{16}	2×10^{12}
Stoichiometry	SiO_2	SiO_2	$SiO_{1.9}$
H content (by IR) as Si-H (at.%)	1-4	<4	None
as SiOH (at.%)	<1	<1	None
Etch rate in 5:1 BHF	<55	22 (7:1 BHF)	140
Refractive index	1.48	1.49	1.46
Stress on Si (10^9 dyne/cm^2) (all compressive)	1.5	3.6	2

Table 3. Comparison of Deposited Silicon Nitride Films

	Laser CVD	Plasma	Hg Photride
Stoichiometry	<SiN	>SiN	Variable
Impurities (at. %)			
H by IR-as Si-H	12	12-16	--
as N-H	11-20	2-7	"typical plasma"
O by ESCA	<5	--	--
Etch rate (Å/sec)	15 (dep. at 425°C)	1.7	12
in 5:1 BOE		(7:1 BOE)	--
No surface photons	44 (dep. at 380°C)	--	--
193 nm photons	8	--	--

Table 4. Summary of the Physical Properties of the Laser Deposited Al, Mo, W and Cr Films

	Deposition Rate (Å/min)	Resistivity (μΩ-cm) bulk	Resistivity (μΩ-cm) film	Percent Carbon in Film	Adhesion, on Quartz (dynes/cm^2)	Tensile Stress (dynes/cm^2)
Mo	2500	5.2	36	<0.9	$>5.5 \times 10^8$	$<3 \times 10^9$
W	1700	5.65	135	<0.7	$>6.5 \times 10^8$	$<2 \times 10^9$
Cr	2000	12.9	210	<0.8	$>5.4 \times 10^8$	$<7 \times 10^9$
Al	1000	2.66	3.0	<4.0	$>5.5 \times 10^8$	$<1 \times 10^9$