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TITLE OF RESEARCH PROJECT: "Photodeposition of Nitride Insulators on III-V Substrates"

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ABSTRACT

We have explored laser assisted chemical vapor deposition (LCVD) of nitride insulators, using an excimer laser operating on either KrF or ArF transitions (248 nm or 193 nm respectively). The properties of silicon nitride films deposited with 193 nm photons on quartz and silicon substrates in a SiH_4, NH_3, N_2 and He mixture are discussed. Aluminum films were deposited at substrate temperatures from room temperature to 200°C using 248 nm or 193 nm photons to dissociate trimethylaluminum (TMA). Deposition of Al films were investigated to isolate problems associated with TMA such as C and O contamination during AlN depositions. The Al film properties were evaluated on SiO_2 and Si substrates. Preliminary results were obtained for aluminum nitride films using TMA and NH_3 as the gas phase Al and N donors. The properties of Cr films deposited over areas >5 cm^2 using 193 nm or 248 nm photons to dissociate $Cr(CO)_6$ have been investigated. Work is currently underway to further characterize AlN and CrN films and to investigate their electrical properties on GaAs and InP substrates.

Photodeposition of Silicon Nitride

The deposition system used for laser assisted chemical vapor deposition (LCVD) of insulators is shown schematically in Figure 1 and described in more detail in references 1, 5-8 in Appendix 1. Laser deposited silicon nitride films have been compared to plasma-enhanced CVD (PECVD) and mercury photo-CVD films. The deposition conditions for LCVD, (PECVD) and mercury photo-CVD of silicon nitride are given in Table 1. The LCVD deposition rate as a function of laser intensity and total pressure are shown in Figures 2 and 3 respectively. The deposition rate increases linearly with average 193 nm power suggesting that at these flows and pressures the deposition of silicon nitride is a single photon first order process. The ratio of NH_3 to SiH_4 absorption cross section at 193 nm is 2×10^{-16} $cm^2/1.2 \times 10^{-22}$ cm^2 and hence NH_3 is the dominant absorbing species. In the limited pressure range from 1.5 to 7.5T the deposition rate increases linearly with total pressure again suggesting a first order process.

The physical properties of LCVD, PECVD and mercury photo-CVD films compared in Table II are similar. The measured adhesion of both PECVD and LCVD films was in excess of 6×10^8 dyne/cm^2 which was the test limit of our apparatus. Pinhole densities for LCVD films are comparable to PECVD films (<1 cm^2) but superior to mercury photo-CVD films.

Chemical properties given in Table III show the LCVD films to be N rich and the PECVD films to be Si rich. An Auger depth profile of LCVD silicon nitride (Figure 4) shows that the stoichiometry is uniform throughout the bulk of the film. The LCVD films lack in terms of etch rates; they etch approximately ten times faster than PECVD silicon nitride. However, at the bottom of Table III the effect of laser surface irradiation ($\sim$0.01 J/cm^2) on the etch rate can be seen. The etch rate was reduced from 44 Å/sec to 8 Å/sec on the

same sample by folding back the transmitted portion of the 193 nm dissociating beam perpendicular to the substrate (Figure 1b). This reduction in the etch rate due to perpendicular irradiation has also been observed in LCVD SiO_2.

The electrical properties of LCVD and PECVD silicon nitride films were compared via aluminum/silicon nitride/silicon MIS capacitor structures. The results of capacitance versus voltage and current versus voltage measurements summarized in Table IV show that the resistivity (measured at 1 MV/cm) and breakdown voltage (measured at 10^{-6} A/cm^2) for LCVD are slightly lower than that of PECVD films. High resistivity and breakdown voltage as well as low pinhole density indicate a low density of incorporated defects on both films. A CMOS digital high voltage switch containing approximately 12,000 transistors using a 5.0 μm minimum design linewidth was used as a vehicle for investigating the feasibility of LCVD silicon nitride as a post metallization cap layer. The yields for the laser nitride were better than the standard phosphosilate glass (4%) or the plasma nitride (12%) cap layer indicating that LCVD films have comparable passivation properties.

Photodeposition of Aluminum and Aluminum Nitride

The experimental arrangement used to deposit Al and AlN films is shown in Figure 1a. An excimer laser was used as the UV photon source (ArF 193 nm, 8 watt at 90 Hz or KrF 248 nm, 10 watt at 90 Hz). A cylindrical lens telescope collimates the laser photons to a beam 2.5 cm wide by 1 mm thick which enters the cell through a quartz window. Helium flowing against the cell windows minimized undesired deposits. The laser beam passed parallel to and approximately 1 mm above the substrate. The temperature of the substrate was monitored by a thermo-couple mounted in the heater/substrate holder, and controlled with a lamp mounted inside of the heater block and a temperature controller.

Aluminum films were initially deposited by flowing hydrogen at 100 SCCM over the trimethylaluminum (TMA 97% purity) with a TMA:H_2 pressure ratio of 1:3. The He flow rate was 70 SCCM and the total pressure was 0.5 T which was maintained by a downstream automatic throttling valve. The best aluminum films were deposited at a substrate temperature of 200°C using 248 nm photons. A lower deposition rate and more carbon incorporation was observed for depositions with 193 nm photons. The deposition rate under these conditions of the Al films ($\pm$5% uniformity across 7.5 cm) was about 1000 Å/min with $\sim$4% carbon and $\sim$7% oxygen (ESCA at CSU) incorporation. The best resistivity measured by linear 4 point probe of the photodeposited Al films was 9.1 μΩ-cm which is close to the bulk Al resistivity of 2.66 μ Ω-cm. Surface inspection of the Al film with a scanning electron microscope shows no signs of voids or hillock formation. Conformal coverage of 5000Å Al films over 4000Å polysilicon steps was observed with no cusping or cracking at the base of the vertical wall. The adhesion of Al to SiO_2 or Si substrates was greater than the limits of the pull tester (6.5×10^8 dynes/cm^2). The stress of photodeposited Al on a Si

wafer was measured by the x-ray technique to be tensile and less than 10^9dyne/cm^2. Improving the long term stability of the aluminum films (formation of Al_2O_3, resistivity) and reducing the carbon and oxygen content is currently being investigated.

Aluminum nitride films were initially deposited at 2T total pressure with 350 SCCM NH_3, 100 SCCM He window purge, and 20 SCCM of He plus TMA gas flows. A low deposition rate was observed for depositions with 248 nm photons while deposition rates of 1000-1800 Å/min were observed for depositions with 193 nm photons. The increased deposition rate at 193 nm may be due to the absorption cross section of NH_3 being larger at 193 nm than 248 nm. The substrate temperature was 220-250°C with delamination of the AlN film from Si substrates occurring at lower temperatures. Depositions were performed with flow ratios of TMA + He:NH_3 1:10, 1:20, 1:50, and 1:100. The refractive index measured by ellipsometry (6328Å) varied from 1.55 to 1.87 which is low compared to reactively sputtered AlN (2.17). An index of refraction of 1.87 was observed for a TMA + He:NH_3 ratio of 1:8 and deposition rate of 1670 Å/min. Lower deposition rates and index of refraction were observed as the ratio of NH_3 to TMA was increased. The composition of the films from ESCA (Colorado State) was 44.6% Al, 24.3% N, and 32% O.

A new vacuum chamber has been designed and fixtured with conflat and VCR feed throughs. The goal being to minimize oxygen contamination in deposited films. The chamber has also been designed to allow for multiple beam depositions (i.e. laser beams and electron beams). The ultimate goal being a comparison, under similar pressure, temperature and gas flow conditions of laser deposited and electron beam deposited AlN films. Work is currently underway to photodeposit AlN films to be sent to NASA Lewis for compositional analysis and to systematically evaluate AlN film properties on Si and GaAs substrates.

Laser Photodeposition of Chromium

Chromium films were deposited on Si and quartz substrates using an excimer laser operating at 157, 193, 248 and 308 nm, which correspond to F_2, ArF, KrF and XeCl transitions respectively. Cr depositions were performed with parallel or normal incidence light. All the substrates were precleaned in HF and deionized water prior to deposition. A reservoir containing chromium hexacarbonyl $Cr(CO)_6$ was connected to the cell and heated 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 was then turned on to preclean the substrate with the UV radiation. A few millitorr of oxygen was introduced into the cell so that the atomic oxygen created by UV dissociation would react with any organic contaminants to form gaseous products such as CO_2, which were pumped out. This step seemed to improve the adhesion of the deposited films. A helium purge of the window was maintained at 70 SCCM. A bright blue or blue-green fluorescence appeared along the path of the laser beam (dissociation volume) through the cell with $Cr(CO_6)$ present. The deposition time varied from 0.5 to 2 min, depending on the thickness desired. Thick (>1μm) Cr films had a tendency to peel when exposed to air. This could be avoided by heating the substrate to about 150 C. The major impurities in the Cr film determined from Auger analysis were about 7% oxygen and 1% carbon. Films deposited with the substrate held normal to the incident laser beam produced metallic Cr, whereas deposition with the substrate parallel or at grazing incidence to the beam produced black powdery films (carbon ~15%). The most carbon free Cr films and highest deposition rates (2000 Å/min) were obtained with normal incidence 248 nm photons. The deposition rate varies with laser power, carbonyl vapor pressure and the deposition area. The uniformity of the photodeposited Cr

over a 2.5 x 2.5 cm area was ±15%. The adhesion of the Cr films were over 5 x 10^8 dyne/cm^2. The stress was tensile and less than 7 x 10^9 dyne/cm^2. The sheet resistivity of the best Cr film on a quartz substrate was 6 ohms/square for a thickness of 3500Å or 210 μΩ-cm. The photodeposited Cr films resistivities were about a factor of 20 higher than the bulk Cr resistivity of 12.9 μΩ-cm. The step coverage was examined for ∿0.5 μm thick Cr films deposited on 0.5 μm polysilicon which was deposited over 1000Å thermal SiO_2 on Si substrates. The films exhibited conformal step coverage with no cracks or thinning at the vertical walls of the steps or voids under the films at the base of the steps. Work is currently underway to deposit CrN using NH_3 as the nitrogen donor.

Summary

In summary we have performed initial deposition and characterization of Al, AlN, Cr and Si_3N_4 films. Deposition of AlN and CrN films with 193 nm photons is currently underway. Cooperative research with scientists at NASA Lewis will be continued to evaluate and optimize these films.

Appendix 1. Publications and Conferences that NASA Lewis was acknowledged.

1. "Photodeposition of aluminum oxide and aluminum thin films," APL 43, 454 (1983).

2. "Electron beam assisted CVD of SiO_2," APL 43, 777 (1983).

3. "Conformal step coverage of electron beam assisted CVD of SiO_2 and Si_3N_4 films," Journal Electrochemical Society, April 1984.

4. "Silicon nitride films deposited with an electron beam created plasma," APL, March 1984.

5. "Comparison of laser and plasma assisted deposition of silicon nitride," ECS, May 8, 1983, San Francisco, CA.

6. "Microelectronic thin film deposition by UV laser photolysis," 15th Conference on Solid State Devices and Materials, September 1983, Tokyo, Japan.

7. "Beam assisted CVD of microelectronic films," MRS, November 14, 1983, Boston, MA.

8. "Thin film deposition by UV laser photolysis," SPIE, January 26-27, 1983, Los Angeles, CA.

9. "Electron beam assisted CVD of silicon dioxide and silicon nitride films," SPIE, January 26-27, 1983, Los Angeles, CA.

Table I. Typical silicon nitride deposition conditions.

	LASER	*PLASMA*	*Hg PHOTOX*
Substrate Temperature	200 < T < 425°C	380°C	150 < T < 200°C
Total Cell Pressure	2 Torr	2 Torr	4 Torr
Gas Flows	10 SCCM NH_3 10 SCCM SiH_4 40 SCCM H_2	21.6 SCCM NH_3 3.1 SCCM SiH_4	$NH_3/SiH_4 = 30$
Deposition Rate	700 Å/min Over 18 cm^2	350 Å/min	65 Å/min
Dissociation Source	λ = 193 nm	450 KHz	λ = 254 nm

Table II. Physical properties of silicon nitride.

	LASER-DEPOSITED		*PLASMA*	*Hg PHOTRIDE*
Substrate Temperature	280°C	425°C	380°C	200°C
Adhesion: Dyne/cm on Si	$>2 \times 10^8$	$>5.5 \times 10^8$	$>6 \times 10^3$	$4-7 \times 10^8$
Pinholes: 50 V Bias in Methanol	Varied	 <1/cm^2 (2000 Å)	2-3/cm^2 (1500 Å) <1/cm^2 (2000 Å)	<5/cm^2 (4000 Å)
Stress: Dyne/cm^2 on Si	Not Measured	~4×10^9 Compr	$3-7 \times 10^9$ Compr. (Reported)	1.4×10^9 Compr. (Reported)
Step Coverage	Good	Good	Good	Good
Density (g/cm^3)	Not Measured	2.4	2.8	Varied

Table III. Chemical properties of silicon nitride.

	LASER-DEPOSITED		*PLASMA*	*Hg PHOTRIDE*
Substrate Temperature	280°C	380°C	380°C	
Stoichiometry	$Si_3N_{4.3}O_{0.08}$		$Si_3N_{3.5}O_{0.03}$	Variable
Impurities:				
H by IR, as Si-H	12%	12%	12–16%	
as N-H	20%	11%	2–7%	Not Reported
O by ESCA	<5%	<5%		
Etch Rate,				
(Å/sec, 5:1 BOE)	200–250	20–50	2–5	12
EFFECT OF SURFACE PHOTONS ON ETCH RATE (Å/SEC) IN 5:1 BOE				
Substrate Temperature	380°C	425°C		
No Photons	44	15		
254 nm Photons	27	9.5		
193 nm Photons	8	6		

Table IV. Electrical properties of silicon nitride.

	LASER	*PLASMA*
ϱ (Ω-cm) @ 1 MV/cm	1.3×10^{15}	3×10^{15}
BV (MV/cm)	2.5	4
k (1 MHz)	7.1	7

Area = 10^{-2} cm^2

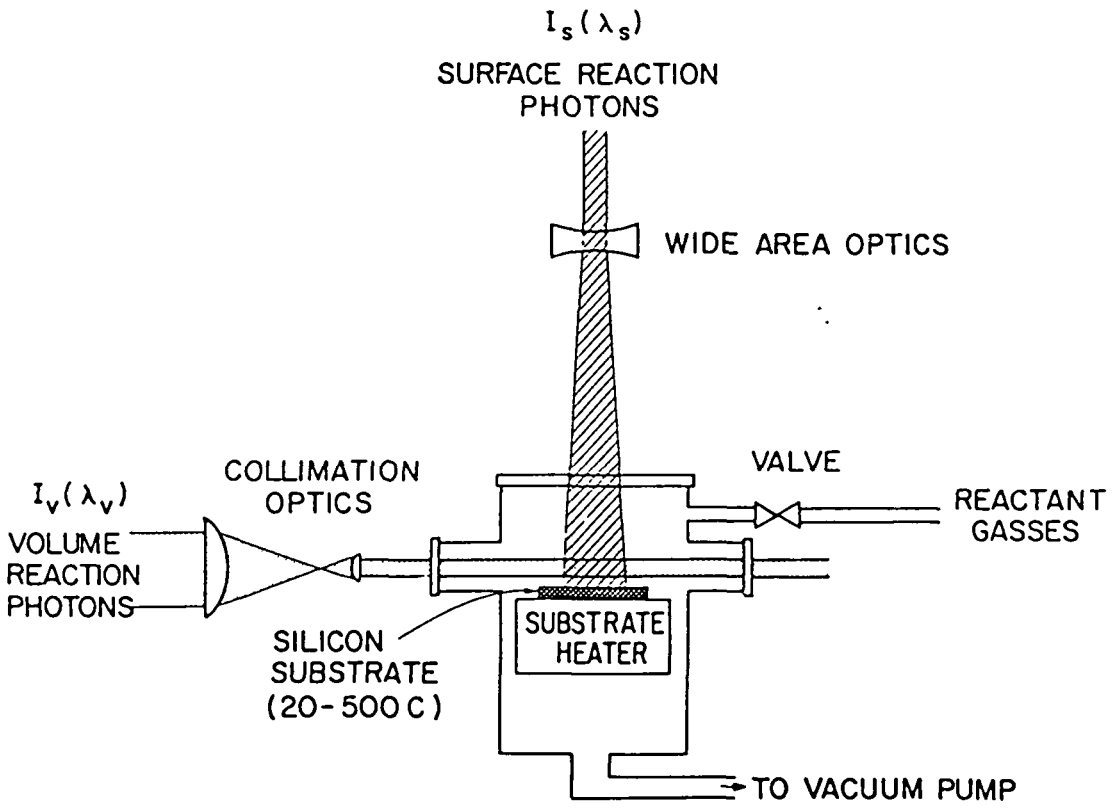

Figure 1a. Photo CVD cell geometry.

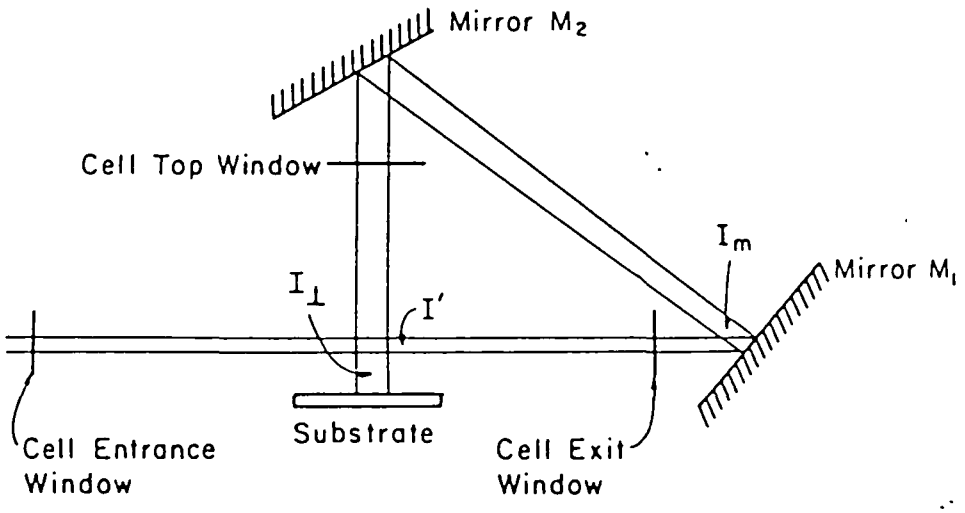

Figure 1b. Optical arrangement for irradiating the sample with surface reaction photons.

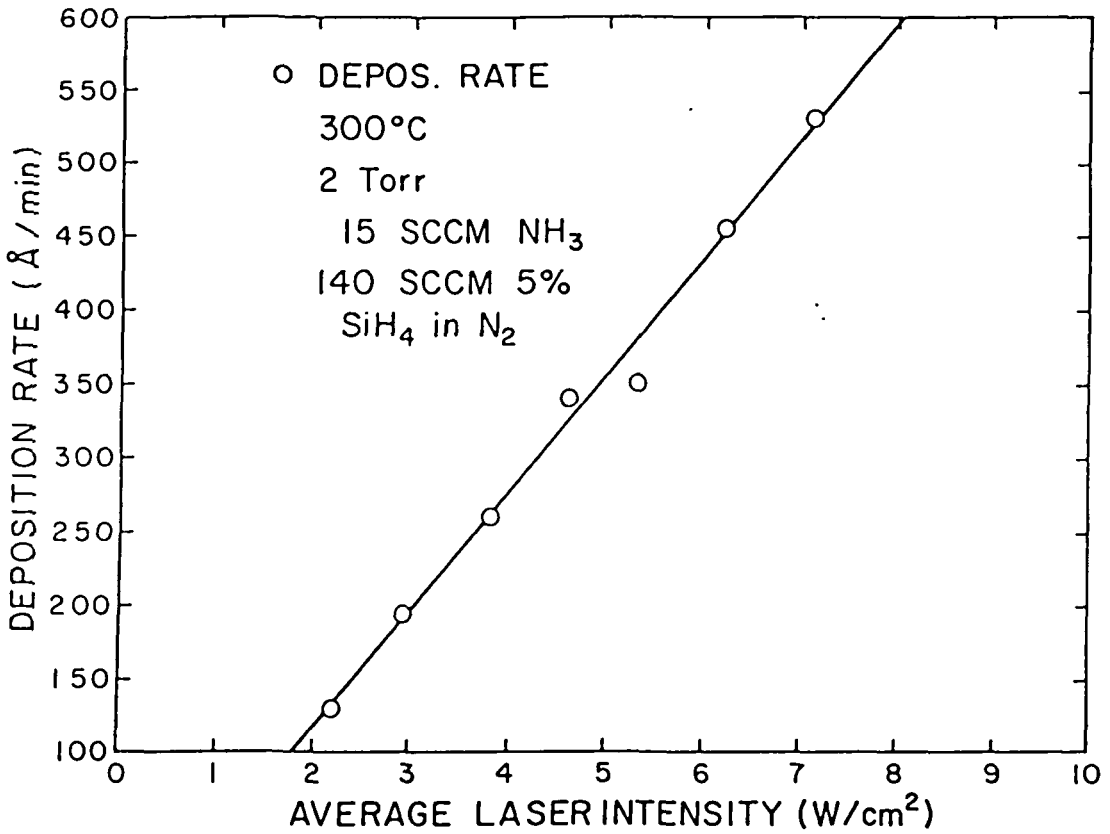

Figure 2. Silicon nitride deposition rate vs. 193 nm photon intensity.

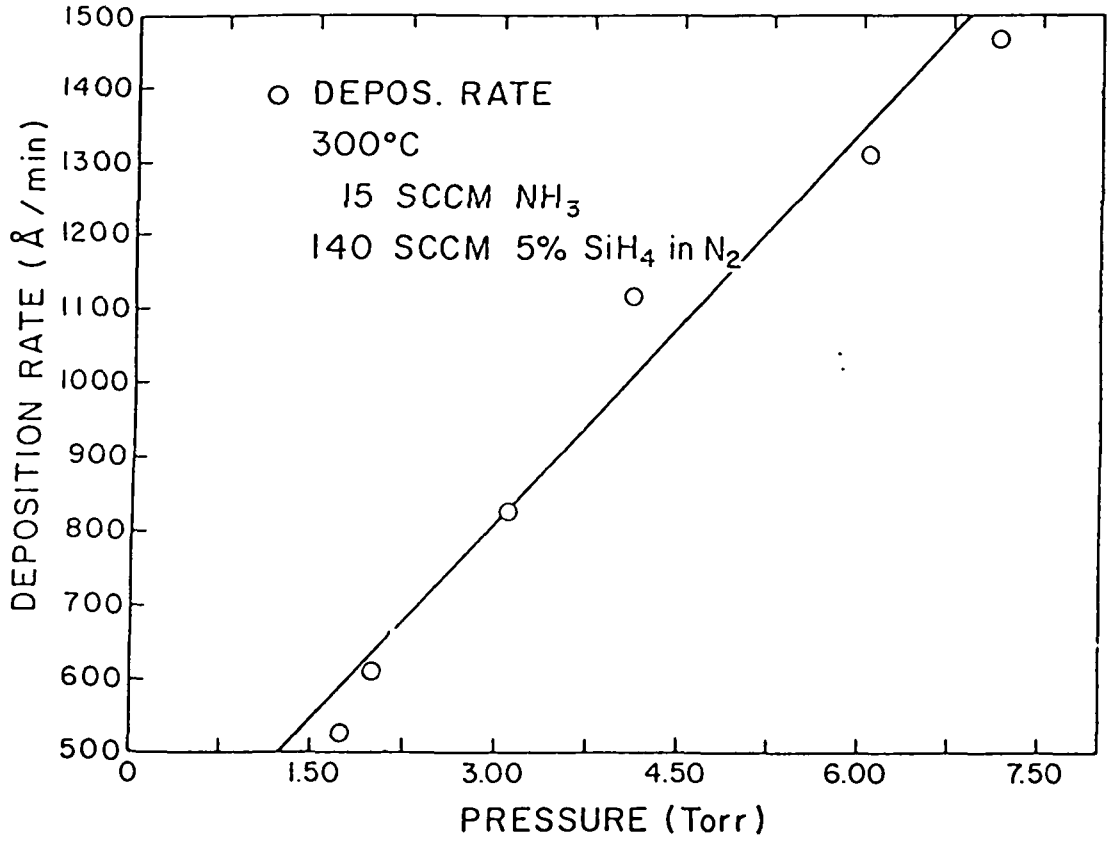

Figure 3. Silicon nitride deposition rate versus total pressure for an average power of 8.5 W/cm^2.

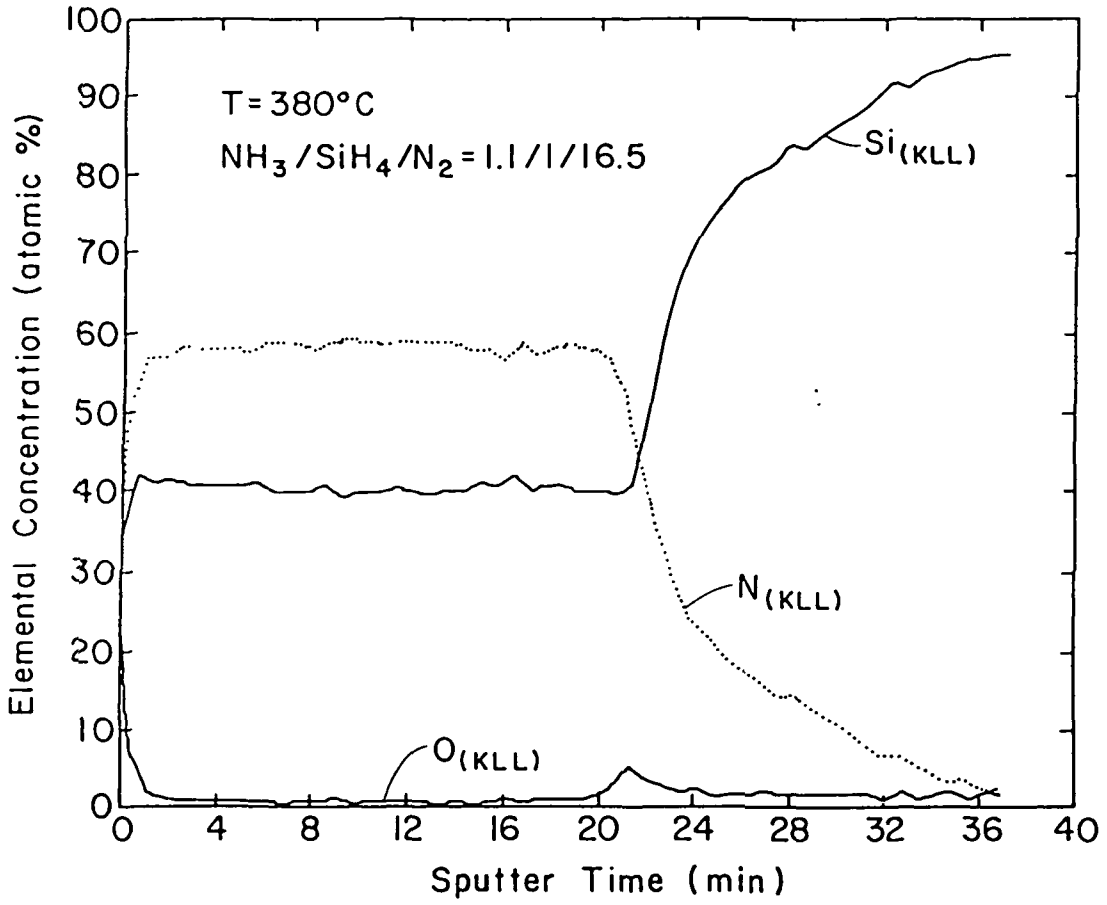

Figure 4. Laser deposited silicon nitride composition.