Monitoring of silicon nitride films grown by PLD using real time single photon-energy ellipsometry.

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Thin films of SiN_x are widely used in the optical and electronic industry due to its dielectric and mechanical properties. In this work, silicon nitride films were deposited on glass and silicon substrates by KrF (248 nm) excimer laser ablation of a Si_3N_4 hot pressed target in an ultra high vacuum system at room temperature. The film growth was monitored by real time ellipsometry at fixed photon-energy (2.5 eV). The different stages of the deposition process were momentarily interrupted to analyze the film in the photon-energy range of $1.5 < hv < 5.0$ eV. The absolute reflectance and spectral ellipsometric parameters are measured to obtain the dielectric function, and the effective medium approximation is applied to estimate the volume composition and film thickness. The ellipsometric results are compared with those of AES and XPS *in situ* characterization.

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I. INTRODUCTION

Heterostructure multilayers have been increasingly used in optics over the last years, some of the most important applications include reflection of extreme ultraviolet (100-1000 nm) and soft X-rays (1-35 nm)[1]. Optics of multilayer coated mirrors have the unique capability of simultaneously allowing high spectral and spatial resolution observations. These properties make them suitable for applications in solar astronomy and molecular microscopy. Multilayer coated mirrors generally consist of alternating layers of low and high atomic number elements [2].

The potential of silicon-based heterostructures in soft X-ray applications is well documented in the literature [3]. Si_3N_4/Si films, for instance, have very low absorption in the 120-250 Å range, in addition to high thermal stability and chemical inertness. Various deposition techniques [3-6] have been used to produce them. In particular, Pulsed Laser Deposition (PLD) looks promising because it satisfies the requirements of selectivity and performance for multilayers fabrication, layer-by-layer growth control. However, the properties of a film-to be-grown are difficult to predict. A slight variation of the deposition parameters (laser fluence, substrate temperature, target-substrate distance, etc.) might result in a profound change of the film properties. The *in situ* monitoring and control of the deposition process is a way to manipulate the composition and optical properties of thin films. Therefore, the thickness control and optical properties evolution using real-time ellipsometry of SiN_x overlayers grown on silicon and glass by PLD is the main object of this application. The deposition rate is also determined with the ellipsometric measurements. This investigation is complemented by the study of the film composition using surface analysis techniques such as XPS and AES.

The experimental setup and procedure are explained in Sec. II. The experimental data obtained by XPS and AES are given in Sec. III a). The ellipsometric measurements are shown in Sec. III b). The discussion of results and final conclusions of this investigation are summarized in Sec. IV.

II. EXPERIMENTAL PROCEDURE

The experiment is based on the photoevaporation of a commercially available Si_3N_4 hot pressed target (Angstrom Sciences, 99.9% purity) placed in a laser ablation system (Riber, LDM-32). The system consists of three vacuum chambers: sample loading, film growth and analysis. Each chamber is independently evacuated by an ion pump, and isolated by UHV gate valves. The growth chamber is equipped with two low birefringence fused silica windows suitable for ellipsometry.

The target is ablated in the growth chamber with a base pressure of 10^{-10} Torr, by a pulsed KrF excimer laser (λ=248 nm, 30 ns pulse width) with an energy of 400 mJ per pulse, corresponding to a fluence of 5 J/cm^2 at the target surface. The laser beam hits the target at an angle of 50 degrees off the surface normal. The maximum chamber pressure is $4x10^{-8}$ Torr during a typical experimental run. The substrates used were polished silicon (111) wafers and glass slides (BK7), which have well documented optical properties [7].

The growth of the films was monitored with a phase modulated ellipsometer (Jobin-Yvon, UVISEL) at a fixed photon-energy (2.5 eV). Spectroscopical ellipsometric analysis was performed at different stages of the deposition process in the 1.5 to 5 eV photon-energy range. Data fitting was carried out using the effective medium approximation (EMA) implemented in the ellipsometer's software [8]. XPS

and AES analysis were realized *in situ* using the adjacent analysis chamber equipped with a Riber-CAMECA Mac-3 system. XPS data were collected by means of Mg-Kα radiation (1253.6 eV) at low, 3 eV, and high, 1 eV, resolution. The AES data were obtained using an electron beam with an incident energy of 3000 eV and a resolution of 3 eV.

III. EXPERIMENTAL RESULTS

a) XPS and AES measurements

The study of the film surface elemental composition was performed by XPS and AES, as shown by Figs. 1, 2, and 3. The chemical composition of the target and film are almost the same, as observed from Fig. 1.

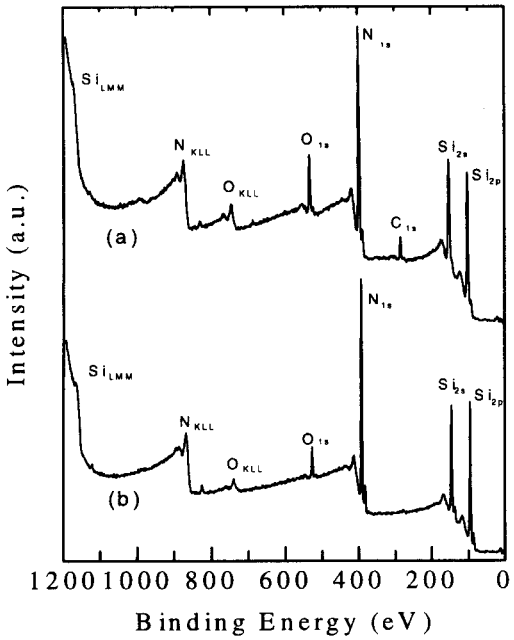

Figure 1.- Comparison of XPS spectra of (a) original target and (b) a typical deposited film.

The only noticeable dissimilarities between these spectra are the complete absence of carbon and the reduction of oxygen in the film, both present as contaminants in the target. The difference in electronic states between target and film is depicted in Fig. 2. The number of electronic states in the target are higher than those in the film, as observed from the FWHM values shown in Fig. 2. A surface scan of the film using AES showing film composition is presented in Fig. 3. The AES and XPS spectra taken from different samples, and several zones in each sample, showed same content of each chemical element.

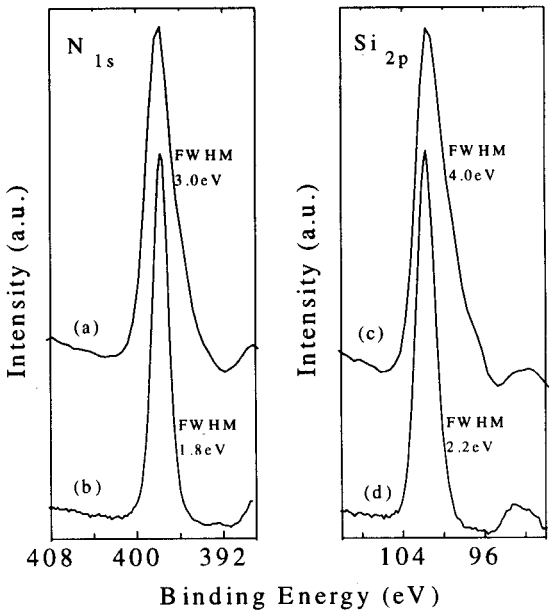

Figure 2.- XPS spectra of the target (a,c) compared to the spectra of a typical film (b,d) for the N (1s) and Si (2p) regions.

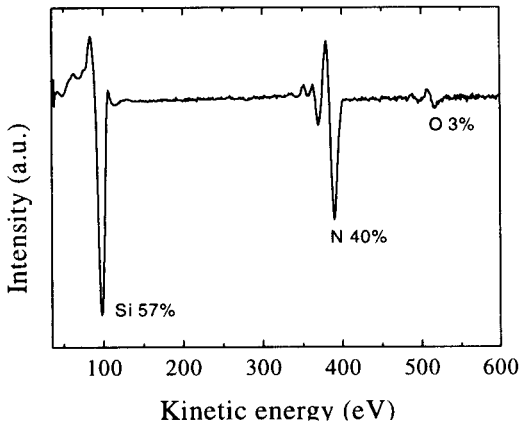

Figure 3.- AES spectrum of the SiN_x film grown on a silicon substrate at room temperature.

b) Ellipsometric measurements

The dielectric function ε is, in general, a function of the photon energy. It is determined by *in-situ* spectro-ellipsometry; that is, by measuring the (ψ,Δ) variables, related with the ratio ρ of the Fresnel reflection coefficients at a given angle of incidence θ_0 by

$$\rho = r_p/r_s = \tan\psi\, e^{i\Delta}$$

The quantities r_p and r_s are the Fresnel reflection coefficients for light polarized parallel and perpendicular to the plane of incidence, respectively. They are strongly dependent on the optical properties of the incident medium, the substrate and the thin film [9].

In the first part of the experiment, ψ and Δ were recorded versus time at a fixed photon energy (2.5 eV), see Fig 4. This procedure represents an excellent monitoring tool to control the deposition rate, film homogeneity and to determine when the deposition process has to be stopped. The next step is to measure the spectral response of both ψ and Δ in the 1.5 to 5 eV energy interval. A routine based on the Levenberg-Marquardt method is used to fit the calculated curves to the experimental data [8]. This routine assumes that the dielectric function of the film, in terms of the photon energy, is the only unknown in the calculation.

The ellipsometric data do not agree with those reported in the literature for a pure Si_3N_4 sample [10]. The best curve fitting is obtained with a mixture of Si_3N_4, polycrystalline Si, p-Si [11], and amorphous silicon, α-Si [12], using EMA [13]. The spectral response showed to be very sensitive to a slight change in the film composition of these three materials. Figure 5 is an example of the spectral curve fitting. The calculated curve uses the film properties reported in ref. 9, and the following values for the relative concentrations: Si_3N_4 (89.5%), p-Si(3.8 %) and α-Si (6.7 %). The film thickness was 1,896Å, and the angle of incidence, 70.5 degrees. The deposition rate was found to be 2.37 Å /seg, which is equivalent to 0.237 Å /pulse.

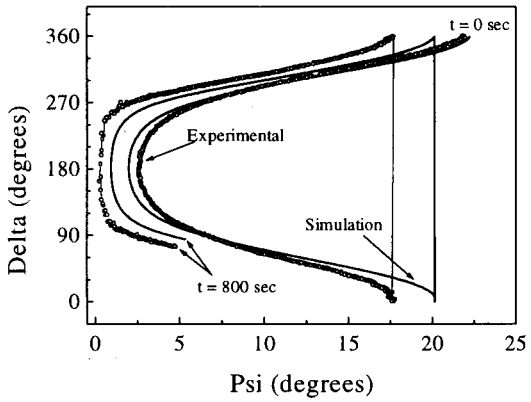

Figure 4.- Experimental trajectory of the SiN_x film evolution plotted in the (ψ,Δ) plane.

Finally, the film deposition evolution is found by fitting the kinetic data using the above mentioned composition. It is the solid curve shown in Fig. 4.

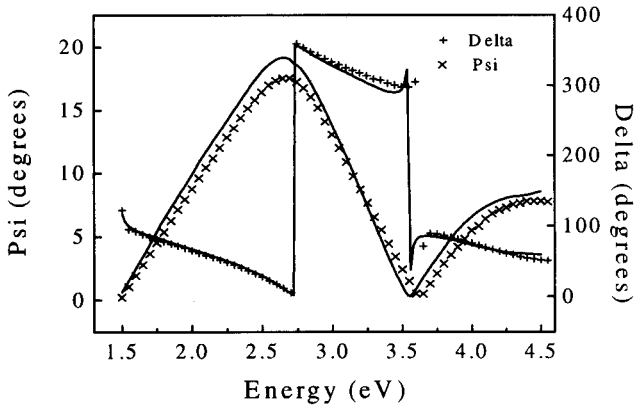

Figure 5.- Best curve fitting (solid line) to the ellipsometric experimental data of the sample spectral response.

Table I summarizes the quantitative analysis obtained by means of all three techniques. The term "ideal concentration" refers to the original stoichiometry of the Si_3N_4 target.

Table I. Quantitative XPS and AES analysis.

	Silicon	Nitrogen	Oxygen
XPS	48.0	52.0	< 1%
Auger	57.0	40.0	3.0
Ellipsometry	51.7	48.3	-
Ideal Concentration	42.9	57.1	0

IV. CONCLUSIONS

A sintered Si_3N_4 target has been ablated by means of a pulsed excimer laser, and the photoevaporated species have been deposited on two different kinds of substrates: Si and glass (BK7). The resultant SiN_x thin films have been grown to a thickness of about 200 nm. They showed no corrugations or fractures, except by a very few droplets which are typical in films processed by PLD. In fact, they resulted to be morphologically smooth and homogeneous as observed by SEM micrographs, not shown here. Good adherence of the films to both kinds of substrates was also noticed, since the deposited films could only be peeled off after scratching their surface with a sharp tip of sapphire or diamond.

The composition and structure of the films have been studied by ellipsometry, XPS, and AES. These results are summarized in Table I. The main observations are: the film composition is substrate-independent, the films did not preserve the original target stoichiometry, they are actually rich in silicon, and a small amount of oxygen was incorporated into them. The oxidation effect can be attributed to target exposure to air prior to film processing.

The target oxide layer is removed after exposing its surface to a few laser pulses.

The stoichiometric difference between target and as-deposited films can be explained by the fact that the gas-phase components of the target ablated species (N, N^+, N_2^+, etc.) are lighter than the solid ones, (Si, SiN, etc.) and easier to pump down or recombine on the deposition chamber walls. The nitrogen content in the films may be enhanced by supplying additional molecular, atomic or ionic species during the actual film processing. This will be done in the near future by implementing a separate plasma source of highly reactive free radical species aimed to the substrate in the deposition chamber. The combined action of two different mechanisms can produce films with a controlled stoichiometry: reaction of solid-phase ablated species with gas-phase dissociated species.

As observed from Table I, the film quantitative analysis by XPS and AES show different results. This can be explained by the fact that AES is an analytical technique more surface sensitive than XPS for most materials, since photoelectrons are more energetic than Auger electrons.

This application also shows that ellipsometry is a powerful too to accurately determine the film thickness and composition. The evaporated material is not pure silicon nitride, as inferred from ellipsometric measurements. The film is actually formed of a mixture of silicon nitride, p-Si and α-Si. The film crystallinity can not be determined either from XPS or AES data. The p-Si and α-Si components change the stoichiometry of the film, and introduce an increment in the absorption of light in the ultra violet region. Therefore, ellipsometry complements and confirms the XPS and AES measurements.

In summary, this work shows that PLD is an attractive technique to deposit SiN_x films. The next step will be to grow SiN_x/Si heterosctructures with the appropriate reflectance in the 120-250 Å range to be used, subsequently, in extreme UV and soft X-ray optics.

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