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Silicon oxinitride and aluminum films interface: Rutherford backscattering and high resolution electron-energy-loss spectroscopic studies

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In this study, we report on the growth and characterization of SiO_xN_y/Al films used as coating for static radiative cooling devices. Aluminum films were deposited by e-beam evaporation in high vacuum conditions. Silicon oxinitride overcoating aluminum was grown by RF reactive plasma sputtering in a mixed oxygen–nitrogen atmosphere. For the Rutherford backscattering spectroscopic (RBS) study, a carbon disc was the substrate. As for the high resolution electron-energy-loss spectroscopy (HREELS) experiments, silicon substrates were used. RBS and HREELS studies showed that the silicon oxinitride/aluminum interface consists of two clearly distinct regions: one is a thin silicon nitride layer and the other one is aluminum oxide. This means that a dynamic phenomenon takes place at the interface. This phenomenon induces oxygen migration towards aluminum. Then the first silicon oxinitride monolayers are depleted in oxygen, leaving silicon nitride and forming a thin film of aluminum oxide.

1. Introduction

The dielectric response of the water vapor and carbon dioxide contained in the atmosphere determines, in the thermal infrared, the so-called "atmospheric window", whose wavelengths range approximately from 8 to 13 μm (i.e. from 770 to 1250 cm^{-1} in wave number units). The low radiance of the atmosphere in this energy range is responsible for the cooling of the earth's surface, observed at night under a clear sky [1]. This radiative cooling effect can be enhanced by using specific emitting material whose emittance is concentrated within the atmospheric window [2]. Still better results will be obtained after intercalating between the emitting surface and the ambient atmosphere, an infrared selective film, reflecting the solar energy, while providing good transparency for infrared radiation. Such devices realize what is called the "inverse green house effect" [3]. In this framework, SiO_2/Al coatings are used for controlling the temperature of satellites in outer space.

According to previous studies, the combination of aluminum and silicon oxinitride films provide a well adapted system for producing and optimizing radiative cooling [4]. The aluminum film serves as reflector and silicon oxinitride is used as the infrared selective film. Silicon oxinitride is a well-known material in the microelectronics industry [5]. However, its use in the radiative cooling framework can be considered as the other main field of application of silicon oxinitride [6,7]. Indeed, both silicon oxide and nitride present strong absorption bands at 1176 cm^{-1} [8] and 875 cm^{-1} [9] respectively. When combining oxide and nitride in silicon oxinitride, these bands broaden and join [10]. Furthermore, the main absorption frequencies of that compound material can be shifted through the atmospheric window, as a function of the oxygen/nitrogen composition ratio. This is the reason why silicon-oxinitride-covered aluminum surfaces are used by many scientists as the basic configuration for ideal radiative cooling devices. Recently, Dereux et al. [11] have proposed a theoretical model for simu-

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lating the reflectivity of multilayer systems. From their results it can be predicted that multilayer structures combining SiO_x and SiO_xN_y films produce interfacial absorption bands that add up to the main absorption bands. Repetitive and periodic configurations of such multilayered systems will provide the best possibility for matching the characteristics of the atmospheric window.

The present work reports about the formation of the interface between silicon oxinitride and aluminum. Due to the different elements present in both films and to their different affinity, dynamical processes between the two layers should be important enough to modify the intrinsic interface structure deep inside the two layers. The goal of this study is to investigate how the phenomena taking place at this interface induce the reorganization of the elements.

The investigation has been performed in two directions: by the Rutherford Backscattering Spectroscopy (RBS) and by the High Resolution Electron-Energy-Loss Spectroscopy (HREELS). RBS is a non-destructive and quantitative technique that allows to probe thick films, to a depth of some micrometers or less. HREELS interface study has been possible with the combination of argon ion sputtering of the film. The study presented here shows that, at the interface, there is an oxygen depletion of the silicon oxinitride layer. The latter becomes pure silicon nitride. Due to the affinity between aluminum and oxygen, the depletion can be explained by the migration of oxygen towards the aluminum film, that oxidizes its top layers. The existence for the formation of pure silicon nitride at the interface is demonstrated by HREELS.

2. Experiment description

2.1. Film depositions

For the RBS experiments, the SiO_xN_y/Al mixture was deposited on polished carbon discs (9.5 mm diameter and 1.6 mm thick). In order to avoid charging effects, the substrates used for HREELS were square pieces (10 mm × 10 mm) cut from doped Si(100) wafers. Before being introduced in the evaporation chamber, the silicon surface was etched with a high pH hydrogen fluoride solution. 1000 Å of aluminum was deposited by means of electron-beam evaporation on the carbon and silicon substrates in an ambiant pressure of 5×10^{-9} Torr. RF sputtering of a silicon cathode in a mixed nitrogen and oxygen plasma was used to deposit 1500 Å of SiO_xN_y on Al/carbon, and 400 Å on Al/silicon substrates, respectively. The residual pressure in the plasma chamber was 8×10^{-8} Torr. The oxygen partial pressure was 10^{-4} Torr. The total pressure of the oxygen/nitrogen mixture was 6×10^{-3} Torr. The plasma was supplied by an RF power generator working at 500 W. The chemical composition of the oxinitride film was determined by RBS and AES as discussed in the following sections. The Al and SiO_xN_y film thicknesses were measured by a quartz crystal microbalance.

2.2. Analysis techniques

The Auger electron spectroscopy (AES) was used to check the film quality and to determine its composition. The measurements were taken at normal incidence, with a cylindrical mirror analyser (CMA) and a coaxial electron gun. The beam energy was set at 2 keV and its intensity at 196 nA. Let us note that the preparation and AES analysis chambers are connected in the same experimental set up, so that samples can be transferred from one chamber to another under UHV conditions [12].

For the RBS experiments, the SiO_xN_y/Al/carbon samples are probed with 2 MeV α-particles produced by a van de Graaff accelerator. The incident beam is normal to the surface while the backscattered particules are collected at 175° and the data are treated as in a conventional RBS measurement [13]. HREELS experiments were performed on SiO_xN_y/Al/Si(100) with a hemispherical spectrometer [14] (type SEDRA ISA-RIBER) in combination with argon ion sputtering. The primary electron energy was 7 eV and the analysis was done in the specular direction at angle of incidence of 45°. A second gun producing a defocalized electron beam of 2 keV energy was used to neutralize the steady detected charg-

ing effect [15]. In a HREELS experiment, one measures surface vibrations that fingerprint the chemical composition of the topmost layers of the sample. In the framework of the dielectric theory of electron energy loss, the dielectric function of a thin film can be extracted from the HREELS spectra, by using an appropriate data treatment [16]. From this information, it is possible to compute the infrared reflectivity of the film and to predict its radiative cooling efficiency.

The sputtering was done with 1 keV energy Ar ions. The experimental setup did not provide a possibility for measuring the ion current impinging on the sample.

3. Results and discussion

3.1. AES

Because of charging effects, no reliable data could be obtained on the overcoated carbon substrates. Fig. 1 shows an AES spectrum recorded on a SiO_xN_y/Al/Si(100) sample. From the analysis of the Si LVV, O KLL and N KLL peaks, the following composition could be deduced for the oxinitride film: $SiO_{1.3}N_{0.6}$.

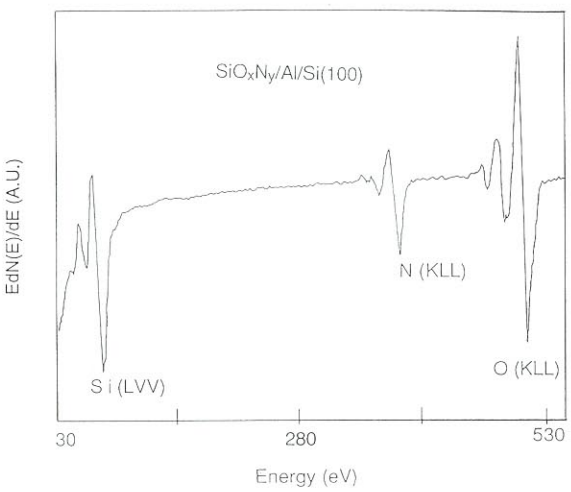

Fig. 1. Auger electron spectrum ($EdN(E)/dE$) of SiO_xN_y/Al/Si(100). From the intensity of the Si LVV, O KLL and N KLL peaks, x and y are measured as 1.3 and 0.6 respectively.

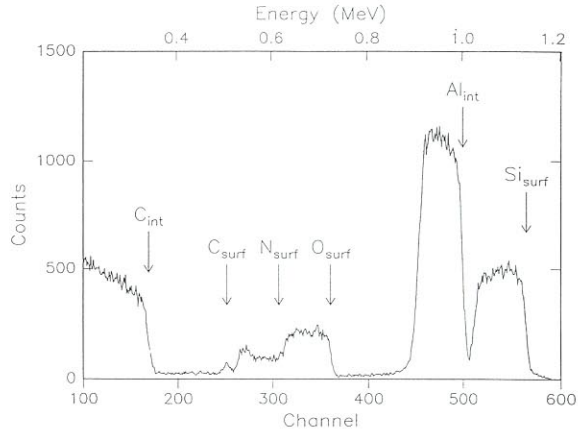

Fig. 2. Rutherford backscattering spectrum of SiO_xN_y/Al/carbon with 2 MeV alpha particles. The composition of the oxinitride film, deduced from the RBS data is $x = 1.3$ and $y = 0.5$.

3.2. RBS

Fig. 2 shows the RBS spectrum of SiO_xN_y/Al/carbon. The arrows labeled with 'surf' indicate the energies where the elements present on the surface should scatter. There are: silicon at 1.126 MeV, oxygen at 0.75 MeV and nitrogen at 0.619 MeV; a small amount of carbon is also at 0.500 MeV and can be explained by contamination of the surface during the ex vacuo transfer of the sample from the plasma chamber to the analysis chamber. The arrows labeled with 'int' indicate the information coming from the interface, that is : aluminum and carbon. From the elemental analysis of the data, the following bulk composition could be determined: $x = 1.33$ for the oxygen concentration, and $y = 0.5$ for the nitrogen concentration, in good agreement with the values obtained by AES. The signal of nitrogen shows an excess of this element at the interface. This should mean that a dynamic process takes place in the first silicon oxinitride layers which changes the composition at the interface. Due to the high affinity between aluminum and oxygen, it is evident that this process consists of a migration of oxygen from the first monolayers of silicon oxinitride towards the aluminum film, to

form aluminum oxide. The reaction of oxygen with the upper aluminum monolayers is confirmed by the shape of the RBS aluminum signal, which shows a gradient of yield height at the interface. The reorganization in the silicon oxinitride is also deduced from the silicon signal which shows a similar yield height gradient from the interface to some monolayers. The signal from the carbon substrate is at 0.35 MeV.

3.3. HREELS

The presentation of the HREELS results will be divided in two parts. First of all we shall discuss the results obtained on the "as-grown" sample, and in a second part we shall analyze the depth profiles obtained after ion sputtering. A HREELS spectrum recorded on the $SiO_{1.3}N_{0.6}$/Al/Si(100) is shown on fig. 3 (lower trace a). The sample surface underwent a slight ion sputtering in order to remove the contamination (mainly hydrocarbons) due to the transfer in air from the plasma chamber to the HREELS spectrometer chamber. The energy resolution was 92 cm^{-1} (11.5 meV) as indicated by the full width at half maximum (FWHM) of the elastic peak. The amorphous nature of the RF-plasma sputtered silicon oxinitride explains the poor energy resolution. The $SiO_{1.3}N_{0.6}$ HREELS spectrum is characterized by three main energy-loss peaks that are due to vibrational excitation of chemical bonds. The first one at 465 cm^{-1} is attributed to the bending vibration of O–Si–O bonds. The second one at 1140 cm^{-1} corresponds to the excitation of the stretching vibration of the same Si–O bond. On the left hand side of this latter peak, one observes a third component at 880 cm^{-1} which is attributed to the stretching vibration of Si–N bonds.

In the framework of the dielectric function theory of electron energy loss [16] it should be possible to provide a quantitative interpretation of this spectrum and, for instance, to determine the oxygen and nitrogen concentrations (x, y) from the analysis of the peak intensity ratios. SiO_2 has a characteristic HREELS loss peak at

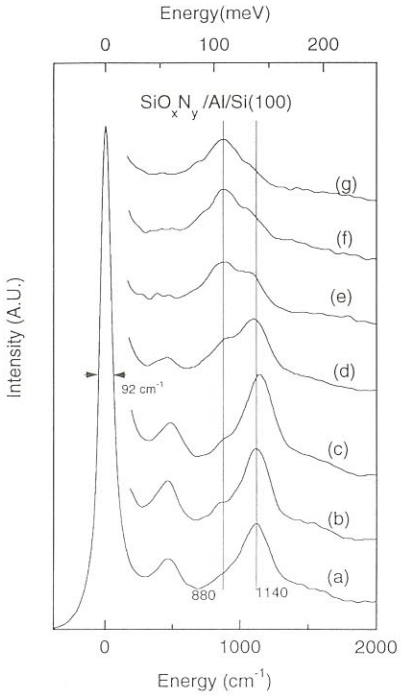

Fig. 3. Sequence of HREELS spectra recorded after successive argon ion sputtering times of $SiO_{1.3}N_{0.6}$/Al/Si(100): (a) sample as introduced; (b) 300 min; (c) 540 min; (d) 740 min; (e) 755 min; (f) 770 min; (g) 810 min. The experimental conditions were the same for all spectra: Electron impact energy 7 eV, angle of incidence 45° and specular geometry.

1176 cm^{-1} [8]. Si_3N_4 has not yet been measured by HREELS, but one can predict than its characteristic loss peak should be observed at a frequency slightly higher than the absorption frequency of 875 cm^{-1}. For the mixed oxinitride compound, one can expect either a one-mode or a two-mode behavior depending on the ionicity of the bonding. If the ionic character prevails, only one HREELS peak will be observed, and according to the model of Chang and Mitra [17] the frequency of this peak will shift almost linearly over the whole intermediate composition range between Si_3N_4 and SiO_2. If, on the other hand, the bonding is of more covalent nature, two distinct peaks (oxide and nitride) will remain, both exhibiting almost linear dispersion versus oxinitride composition. Such a two-mode behavior has

been reported and quantitatively analyzed by HREELS for AlGaAs ternary alloys [18].

The two-mode behavior was reported for oxinitrides in a previous HREELS study by Ronda et al. [10]. It is confirmed here by the presence of separate oxide and nitride related peaks in spectrum a of fig. 3. However, due to the amorphous character of the oxinitride film and to the poor resolution of the spectra, it is not possible to go further into a quantitative analysis of the data. Indeed, all available theoretical models including the dielectric theory are strictly relevant to crystalline compounds only and they may not apply to our case.

In the configuration of our HREELS experiments, a layer thickness of about 100 Å is probed under the surface of the sample. Argon ion sputtering had to be used in order to get a depth profile of the film and to reach the aluminum interface. Unfortunately, due to the instability of the ion gun and to the impossibility of measuring the ion current on the sample, no reasonable estimate can be proposed for the sputtering yield so that the results can be discussed only qualitatively. Fig. 3 (traces b to g) shows HREELS spectra recorded after successive sputtering times that are indicated in the caption. After 300 min ion bombardment (spectrum b), no significant difference is observed in the loss peak positions and intensities. This is an important result, because it means, on one hand, that the homogeneity of the film is good, and, on the other hand, that the sputtering process does not affect the stoichiometry of the oxinitride film. After 300 min, the loss peak at 880 cm^{-1} appears clearly and becomes more and more intense, while the loss peaks at 465 and 1140 cm^{-1} start decreasing in intensity. This indicates that one has reached a depth where silicon oxinitride is gradually replaced by silicon nitride. Indeed, the last spectrum (g) of fig. 3 corresponds unambiguously to the fingerprint of pure silicon nitride. The observed Si–N stretching peak position is close to the expected value of 880 cm^{-1}.

There is also a shoulder peak developing at 650 cm^{-1} visible on spectra (f) and (g) of fig. 3. This peak, which has been observed by Strong et al. [19] after oxygen adsorption on Al(111) is assigned to a precursor aluminum oxide species and indicates the proximity of the aluminum interface.

4. Conclusion

Two ways of investigating the SiO_xN_y/Al interface were presented. Obviously these two ways provide complementary and convergent information to understand the dynamics taking place at the boundary of the films. RBS shows an excess of nitrogen and, from the shape of the aluminum and silicon yield signals, predicts an important physical and chemical activity at this interface. HREELS shows, after long argon sputtering, the transformation of the silicon oxinitride to silicon nitride. In keeping with the RBS results, HREELS indicates the presence of an intermediate layer of pure silicon nitride at the interface. This means that due to an efficient process, oxygen migrates from the silicon oxinitride, to the adjacent aluminum layers, completely depleting those silicon oxinitride layers close to the interface.

The results described above have two main important consequences. The first one concerns the optical predictions done by many models of infrared selective devices, that always consider the interface as a non interactive medium. The second one is about the formation of pure silicon nitride and probably of aluminum oxide induced by oxygen diffusion at the SiO_xN_y/Al interface.

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