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Compositional analysis of silicon oxide/silicon nitride thin films

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Hydrogen, amorphous silicon nitride (SiN_x:H abbreviated SiN_x) films were grown on multicrystalline silicon (mc-Si) substrate by plasma enhanced chemical vapour deposition (PECVD) in parallel configuration using NH_3/SiH_4 gas mixtures. The mc-Si wafers were taken from the same column of Si cast ingot. After the deposition process, the layers were oxidized (thermal oxidation) in dry oxygen ambient environment at 950 °C to get oxide/nitride (ON) structure. Secondary ion mass spectroscopy (SIMS), Rutherford backscattering spectroscopy (RBS), Auger electron spectroscopy (AES) and energy dispersive X-ray analysis (EDX) were employed for analyzing quantitatively the chemical composition and stoichiometry in the oxide-nitride stacked films. The effect of annealing temperature on the chemical composition of ON structure has been investigated. Some species, O, N, Si were redistributed in this structure during the thermal oxidation of SiN_x. Indeed, oxygen diffused to the nitride layer into Si_2O_2N during dry oxidation.

Keywords: *SiN_x:H; oxidation; PECVD; annealing temperature; elemental analysis*

1. Introduction

Amorphous silicon nitride films are known to be very useful for different aspects in materials science. These films are used as an excellent material for technological applications [1], including solar cells [2], radiative cooling [3], gate dielectric [4], etc. Silicon nitride (SiN_x) films can be deposited by different CVD techniques. PECVD is one of the methods most often used. The use of SiH_4 as a silicon source and NH_3 as a nitrogen source produces commonly a substantial amount of hydrogen (>10 at.%) in the films, forming Si–H and N–H bonds [5]. Amorphous films grown by PECVD at temperature in the range of 300 °C to 400 °C have almost stoichiometric composition (Si_3N_4). Oxidation of SiN_x depends on temperature, atmosphere type and physical properties of the oxide layer [6]. As thermally grown layers, silicon oxide (SiO_2) is obtained by a long-time energy-intensive high temperature process (∼1000 °C) [7]. Oxide/nitride (ON) structure is considered as a good structure for passivation and antireflection coatings (ARC) in solar cells [8, 9]. The oxidation product nucleates and grows laterally to produce a continuous film on the surface. The nuclei growth is due to the oxygen adsorbed on the SiN_x sample surface causing simultaneously oxygen depletion in the zone around each nucleus and inhibiting the nuclei formation. The literature shows some databases about SiN_x oxidation in different test conditions [10]. Du et al. [11] verified that the oxidation process of SiN_x is limited by the reaction kinetics and not by the mass transport. When silicon nitride is oxidized by O_2 diffusion, a damaged zone is formed at the nitride-oxide interface. This phenomena accelerates the oxidation [12], which occurs in three stages: (i) oxygen adsorption on the surface of nitride; (ii) oxygen nucleation at the interface; (iii) growth of oxide layer. The oxidation of PECVD grown SiN_x obeys a parabolic law as a function of time, similar to silicon oxidation.

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The chemical composition of each layer needs to be determined precisely because the electrical properties of the dielectric films depend on the chemical composition of each layer in the ON structure. However, it is very difficult to determine the precise stoichiometry of each layer in the ultra-thin oxide-nitride films, because of experimental uncertainties due to surface roughening, preferential sputtering effect for depth profiles, different Auger electron escape depth for each element and actual interface width [13].

The purpose of our investigations is the use of four complementary analytical ion beam techniques to study the ON structure. We report on a comparative compositional analysis of oxide-nitride films obtained through thermal oxidation, by four different methods based on X-ray, electron and ion scattering. In particular, energy dispersive X-ray spectroscopy (EDX), Auger electron spectroscopy (AES), Rutherford backscattering spectroscopy (RBS) and secondary ion mass spectroscopy (SIMS) were used. These methods are different not only in their physical principle but also with respect to several practical aspects. For example, EDX and AES require calibration and, therefore, appropriate standards are necessary, whereas RBS provides quantitative composition data directly. SIMS analysis is commonly used in oxide-nitride film depth profiling [14–16] and particularly to quantify very light elements such as hydrogen. However, quantitative nitrogen distribution with subnanometer depth resolution is still an analytical challenge. The experimental details are given in Section 2. Section 3 presents the experimental results obtained from SIMS, RBS, AES and EDX measurements. Finally, major results of this work are summarized in Section 4.

2. Experimental

In this work we used Heat Exchange Method (HEM) multicristalline Si (mc-Si), 10 cm × 10 cm wafers, 350 μm thick, boron doped, p-type, 1 Ω·cm resistivity. All the samples having a similar crystal structure were taken from the same column of an ingot. Front polished Cz-Si wafers, p-type, (1 0 0) oriented, 2 Ω·cm resistivity were used only for investigation by ellipsometry. The wafers were cleaned by etching in dilute hydrofluoric acid for removing organic contaminations and native oxide, rinsed in deionized water and dried with nitrogen. Then, SiN_x film was immediately deposited on the Si substrates in a PECVD system. The precursor gases used were of ultrahigh purity electronic grade SiH_4 and NH_3. Electronic grade mass flow controllers allowed independent control of all gas flow parameters. The vacuum system provided a residual pressure of about 133 mPa. The flow gas ratio $R = NH_3/SiH_4$, the deposition pressure, deposition time, temperature and the plasma power were kept constant at 6, 227 Pa, 160 s, 380 °C and 4.6 kW, respectively.

In this experiment, SiN_x films were oxidized in dry oxygen at 950 °C in a controlled O_2 atmosphere to obtain the final ON structure. Refractive indices and thicknesses were measured by a single wavelength (632.8 nm) ELX-02 C DRE ellipsometer employing He–Ne laser beam at an angle of 70°.

For SIMS depth profiling, IMS4FE7-CAMECA instrument was used. The primary bombarding beam source was Cs^+, and secondary ions were monitored for each species of interest (in this case, N, O, H and Si). Primary beam impact energy of 15 keV, incidence angle of 24°, and depth resolution less than 2 nm were the conditions used in this analysis. Nitrogen and oxygen and hydrogen profiles were quantified using suitable standards. The relative sensitivity factor (RSF) obtained in the analytical conditions was 2.37×10^{16} at/cm^3. The sputtering rates for each element were about: 8.779 Å/s, 9.279 Å/s and 9.103 Å/s for nitrogen, oxygen and hydrogen, respectively.

Rutherford backscattering (RBS) was used to determine the Si, N and O atomic concentrations, as well as the density of the nitride and oxide in the samples. The Van der Graaf tendem accelerator was located in the Centre de Recherche Nucléaire d'Alger (CRNA) and equipped with a 2 MeV He^{2+} ion beam. Incident beam hit the sample at incidence angles of 70° and 0° (as referred to the normal of the surface), the detection angle of 170° and the current of 50 nA were used. After

the background correction, the experimental spectra were simulated using the SIMNRA program [17] to determine the stoichiometry and the areal density. The parameters set included the elements concentrations (except that of hydrogen).

AES measurement was performed with a cylindrical mirror analyzer with an energy resolution $\Delta E/E = 0.6$ %. The energy of primary electron was 5 keV. The Auger spectra were recorded in the derivative mode. In order to check the homogeneity of the film composition, depth profiling was carried out by alternating measurements of Auger spectra and sputtering the sample surface with 4 keV Ar^+ ions.

Energy dispersive X-ray (EDX) spectra were recorded with a scanning electron microscope (Philips ESEM-XL30-FEG) equipped with a field-emission cold cathode as an electron source and a Si (Li) X-ray detector. Typically, the electron accelerating voltage was 5 keV and the detection take-off angle 35°. The correction was applied to determine the relative atomic fractions of the three components N, O and Si. Hydrogen could not be detected by this method.

3. Results and discussion

SIMS was used to confirm the presence of desired elements and the absence of undesired elements such as carbon impurities, and also to demonstrate that the elemental content was homogeneous throughout the ON structure. Fig. 1 shows the SIMS results for an ON sample annealed at 700 °C for 30 min in nitrogen ambient atmosphere. Silicon, oxygen, nitrogen and hydrogen signals, also reported, prove the presence of these elements in the ON structure. Thanks to SIMS analysis we could identify the different layers existing in the ON structure. We found the thickness of 0.037 µm, 0.069 µm and 0.006 µm for SiO_2, SiN_x and Si_2O_2N, respectively.

Ellipsometric measurements of thickness (e) and refractive index (n) of as deposited layers gave e = 80 nm, n = 2 for silicon nitride and e = 40 nm, n = 1.47 for silicon oxide. The thickness of SiN_x layer has been reduced from 80 nm to 69 nm after oxidation and heat treatment at 700 °C.

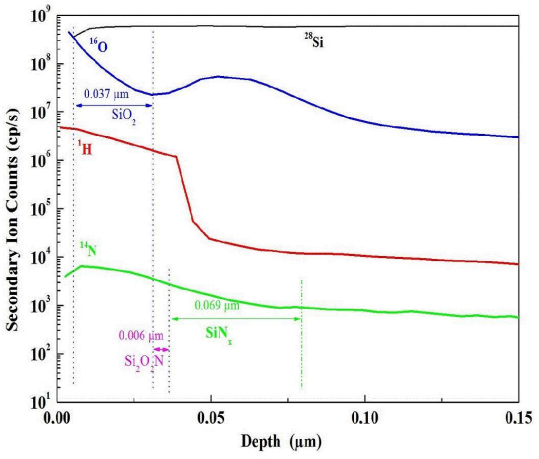

Fig. 1. Depth profiles of Si, O, N and H in an ON structure annealed at 700 °C.

Fig. 2 depicts the SIMS oxygen depth profiles for several samples as-deposited and annealed at different temperatures. As shown in the figure, remarkable oxygen tails are found as secondary ion as a result of 15 keV Cs^+ ion sputtering. From the SIMS measurements, we have found high-oxygen content on the surface. Indeed, this was due to the oxidation growth effect on nitride [18]. We observed a pile-up of oxygen at the SiO_2/SiN_x interface at the depth around 0.05 µm that forms the oxynitride phase.

The Si_2O_2N species come from broken bonds that exist as an intermediate phase between the SiO_2 and the SiN_x. However, a form of a complete distribution could be derived directly from the distribution of respective quasi-molecular ions. So, we think that Si_2O_2N can exist in the silicon oxide-silicon nitride interfaces. The SiN_x and the SiO_2 phases never coexist in the bulk under equilibrium conditions. They are always separated by silicon oxynitride, Si_2O_2N [13].

Fig. 3 presents a joint plot of Si/N versus depth at different annealing temperatures as calculated from the data obtained by SIMS. The data points refer to the ON sample oxidized at 950 °C by dry oxidation. As shown in Fig. 3, again an excess of silicon component is observed. This can

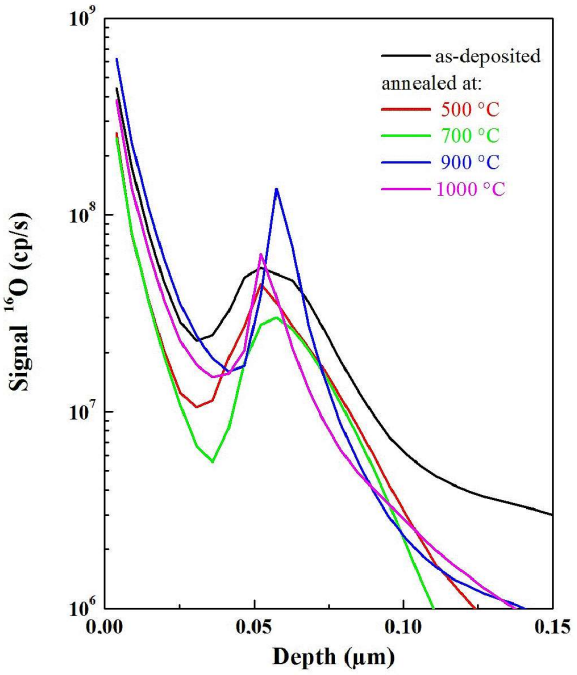

Fig. 2. SIMS depth distribution of oxygen concentration for samples annealed at different temperatures.

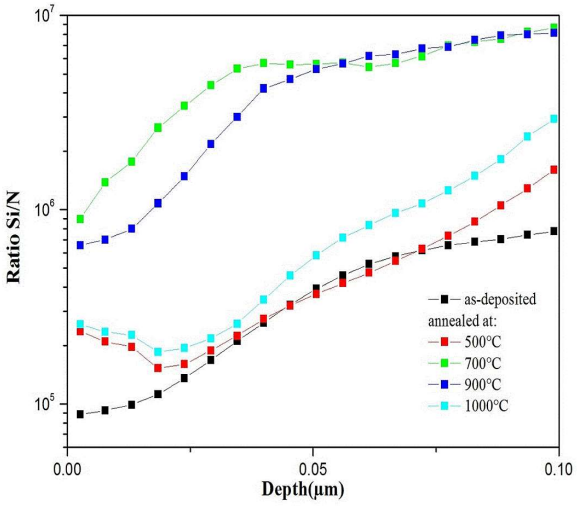

Fig. 3. SIMS depth distributions of Si/N ratio on ON structure for as-deposited and annealed at: 500 °C, 700 °C, 900 °C and 1000 °C.

be explained by the fact that the signal of Si is higher than that of N in every annealing temperature. In the range of depth between 0 and 0.50 µm, we can see that Si/N ratio increases when the annealing temperature increases from as-deposited to 700 °C.

However, beyond 700 °C, the Si/N ratio decreases. This is probably due to low amount of Si atoms and the recoiled nitrogen atoms during Cs^+ ion sputtering that are affected by the high annealing temperature.

SIMS analysis of the oxide/nitride films suggests that the resulting profile of oxygen/nitrogen concentration ratio (Fig. 4) yields one large peak near the dielectric surface of SiN_x. This is due to the presence of silicon oxynitride thin film in this region. When the annealing temperature increases, the O/N ratio increases with annealing temperature up to 900 °C. Indeed, when the temperature of annealing step increases, the oxidized dielectric film becomes larger. So, more oxygen is incorporated into the dielectric film, and therefore, the oxygen atoms substitute the nitrogen atoms which induces the formation of thin silicon oxynitride layer [19].

The chemical composition of each layer needs to be determined precisely because the electrical properties of the dielectric films depend on the chemical composition of each layer in the ON structure. Hong et al. [20] determined that there is a direct correlation between the mass density of SiN_x films and the concentration of Si–N bonds, as determined by FT-IR. In the meantime, Weeber et al. [21] have shown that the maximum Si–N bond concentration corresponds to stoichiometric SiN_x (Si_3N_4) with the refractive index in the vicinity of n = 2. Some authors reported that high surface passivation quality could be maintained for ARC SiN_x or double antireflection coating (DARC) SiO_2/SiN_x after annealing in forming gas atmosphere. Fourier transformed infrared absorption measurements revealed a strong dependence of the annealing temperature on the stability of Si–N bonding density. The passivation quality after the firing process depended strongly on the Si–H bonding density. Jehanathan et al. [22], and Lelièvre et al. [23] stated that the annealing leads first to breaking Si–H bonds which are less thermally stable than N–H (bond energy Si–H and N–H are 3.1 eV and 4.1 eV, respectively).

The general trend is that the hydrogen content in the stacks decreases with increasing annealing temperature.

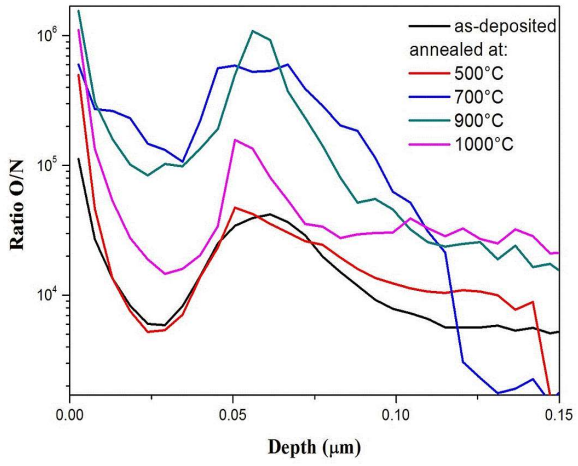

Fig. 4. SIMS depth distributions of O/N ratio for as deposited and annealed films at temperatures 500 °C, 700 °C, 900 °C and 1000 °C.

Additionally, the global composition of the films in ON structure was determined by Rutherford backscattering spectrometry (RBS) using a 2 MeV He^{2+} beam. The spectra were analyzed using SIMNRA simulation program [17]. Experimental data as well as simulation results are shown in Fig. 5 for a SiO_2/SiN_x sample. The simulation reproduces correctly the experimental signal of the sample. We have found by the RBS analysis that the silicon nitride layer deposited by PECVD with R $(NH_3/SiH_4) = 6$ is stoichiometric Si_3N_4. On the other hand, thermal oxidation also gives stoichiometric silicon oxide SiO_2.

The concentration profile for Si, N and O atoms derived from the background-subtracted data and the obtained results (figure not shown) as a function of annealing temperature show that silicon and oxygen concentrations increase with annealing temperature. However, nitrogen concentration decreases as annealing temperature increases. This behavior can be correlated with the results obtained by SIMS.

We have used AES in order to check the homogeneity of the ON structure [24]. AES spectra have been collected for the sample annealed at 700 °C

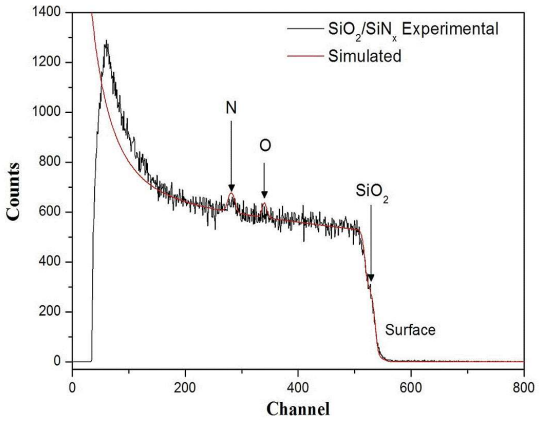

Fig. 5. Typical RBS spectrum of ON structure recorded with He^{+2} ions at 2 MeV. Simulation by SIMNRA is given for comparison. Chemical symbol arrows are given to show the signal of each element located at the film surface.

during 30 min in N_2 atmosphere (Fig. 6). The spectra have been normalized and show that the sample contains oxygen and nitrogen in the amounts in agreement with SIMS and RBS data. This spectrum is related to the interface region. In this region, O comes from a superficial oxidation of silicon nitride and this region reveals a presence of low intensity N KLL peak.

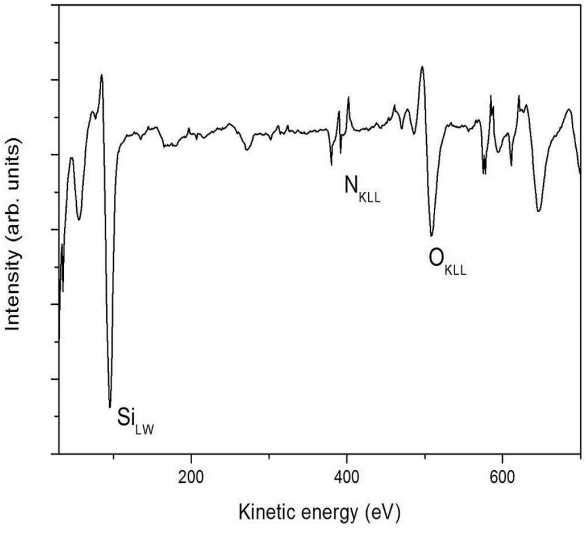

Fig. 6. First derivative AES survey spectrum of oxide/nitride film obtained after dry oxidation of SiN_x and annealed at 700 °C during 30 min.

The SiN_x oxidation as a function of annealing temperature has been explained by assuming that the oxidant species diffuses towards the SiN_x/oxide interface where it reacts with the silicon nitride. In addition, it is considered that under steady state conditions the flux of oxygen is constant at any point in ON system. Something that remains as unknown is the actual chemical reaction occurring during oxidation.

A typical EDX spectrum of oxide/nitride film is shown in Fig. 7. Typically, the electron accelerating voltage was 5 keV and the detection take-off angle was 35°. Fig. 8 presents a joint plot of X = N/Si and X′ = O/Si calculated from the data obtained by EDX versus annealing temperature. The data points refer to the sample of SiN_x series deposited with R = 6 and oxidized at 950 °C during 3 hours.

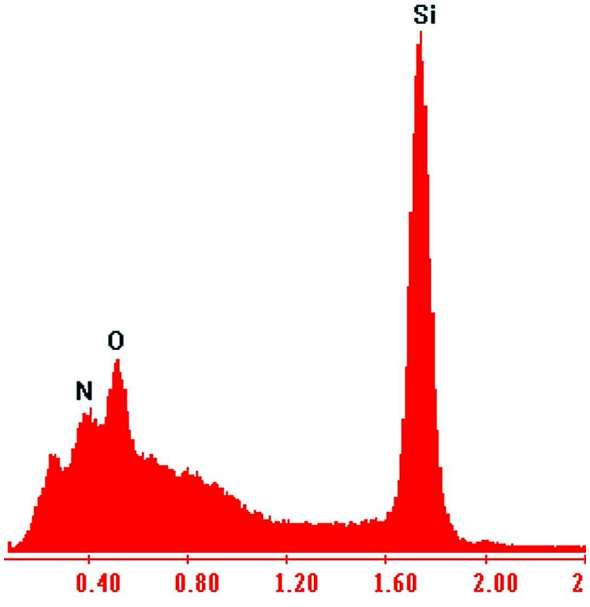

Fig. 7. The EDX spectrum of a typical oxide/nitride film with similar amounts of nitrogen and oxygen. Electron beam energy: 5 keV and the detection take-off angle 35°.

Although EDX does not deliver information on hydrogen, the other components (Si, N, and O) can be readily analyzed with sufficient accuracy if well certified reference samples are also available for the intermediate composition ranges.

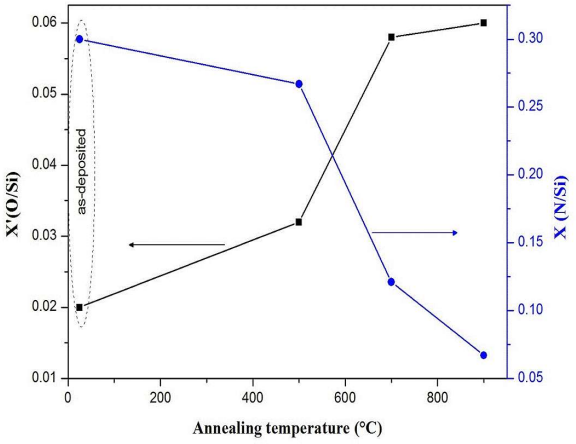

Fig. 8. Correlation between O/Si and N/Si with annealing temperature determined by EDX in oxide/nitride film oxidized at 950 °C during 3 hours. The SiN_x films were deposited by PECVD with R = 6.

It should be noted that there is a similar tendency in the variation of O/Si and N/Si between EDX and RBS measurements. In both analyses, we have found that the O/Si increases with annealing temperature, whereas N/Si decreases. The RBS measurement confirms that the O/Si and N/Si determined by EDX are credible. The higher the annealing temperature the higher the incorporated amount of oxygen in the structure.

4. Conclusion

In this work, we determined the composition of silicon nitride (SiN_x) films oxidized in dry oxygen at 950 °C. Silicon nitride was obtained by PECVD from a mixture of gases SiH_4 and NH_3. The annealing temperature used in the treatment of the oxide/nitride film had a strong influence on the composition of the ON structure. Reasons of this variation should be found in the atomic composition that has been determined by SIMS, RBS, AES and EDX. The SiN_x layers prepared with R = 6 have a stoichiometric Si_3N_4 structure. Likewise, the oxidation of SiN_x leads to growing of silicon oxide with stoichiometric SiO_2 structure. It should

be mentioned that the ratio of N/Si decreases with annealing temperature while the O/Si ratio increases. So, more oxygen is incorporated into the dielectric film, and therefore, the oxygen atoms substitute the nitrogen atom which induces the formation of thin silicon oxynitride layer.

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