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Concentration and depth profiles of elements in $Si_xN_yH_z$/Si thin films produced by PECVD

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Abstract

Plasma enhanced chemical vapor deposition (PECVD) with SiH_4/NH_3 mixtures was used to produce silicon nitride thin films on silicon substrates. These types of films are commonly used as dielectrics in modern semiconductor technology; however, the incorporation of large amounts of hydrogen affects negatively their stability and electrical properties. Therefore, quantifications of the hydrogen content and chemical composition of these films are required. Forward elastic scattering using a 10 MeV $^{12}C^{3+}$ beam was used to determine the thickness and stoichiometry of the films. Nuclear reaction analysis (NRA) using a 0.825 MeV deuterium beam was also applied to measure the low concentrations of oxygen and carbon in these films. The chemical structure of the silicon nitride layers was studied using infrared spectroscopy.

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Keywords: Elastic forward scattering; Rutherford backscattering; Elastic recoil detection analysis; IBA techniques

1. Introduction

Thin films of silicon nitride have been prepared and studied for many years [1], since this is a promising material for technological applications, including solar cells [2], radiative cooling [3], gate dielectrics [4], dielectrics for providing electrical isolation between contiguous metallic conduction lines in modern integrated circuits [5], etc. Most of these applications require the preparation of silicon nitride thin films at low temperatures (<350 °C) to avoid inter-diffusion between adjacent layers of devices. PECVD is one of the methods most used to prepare silicon nitride films. However, the common use of SiH_4 as the silicon source and NH_3 as the nitrogen source produce a substantial amount of hydrogen (>10 at.%) in the films, forming Si–H and N–H bonds [6]. The composition and properties are strongly affected by the presence of hydrogen, which lowers the chemical and thermal stability, degrading the electrical properties of the films and causing severe reliability problems when they are used in electronic devices.

In this work, IBA was used to measure the elemental composition of silicon nitride films on silicon substrates, deposited by PECVD using several SiH_4/NH_3 mixtures. A major requirement of the analysis is the determination of the total elemental composition profile including the hydrogen content, which is a by product of the deposition process. The sensitivity of the RBS methods is low for light elements in heavier substrates and it cannot be applied to detect hydrogen. In these cases, conventional elastic recoil detection analysis (ERDA) using a $^4He^+$ beam [7], and a combination of RBS/ERDA for simultaneously measuring $^4He^+$ backscattered particles and the hydrogen forward

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recoils are often used [8]. In this work, elastic forward analysis (EFA) [9] using a $^{12}C^{3+}$ beam was applied to determine the elemental composition and thickness of $Si_xN_yH_z$ films. Oxygen and carbon are the most frequently found contaminants in these films. Nuclear reaction analysis (NRA) using a $^{2}H^{+}$ beam was applied to measure the low concentrations of O and C incorporated in the films. Infrared spectroscopy (IR) was used to study the nature of the hydrogen bonds (Si–H and/or N–H) and the chemical structure of the silicon nitride layers.

2. Experimental

PECVD was used to fabricate the amorphous silicon nitride thin films on polished silicon wafers (4 in. in diameter, n-type, ⟨1 0 0⟩ crystal plane, dc resistivity 3–5 Ω cm, and thickness 525 ± 25 μm). The films were prepared in a radial flow reactor with reactant gases SiH_4–NH_3, and nitrogen as carrier gas, under the following conditions: substrate temperature: 300 °C, signal frequency: 100 kHz, chamber pressure: 210 mTorr. With the aim of studying the film production parameters, six samples were prepared by changing the $R = NH_3/SiH_4$ gas flow ratio as follows: 1.75, 2.35, 2.91, 3.45, 3.92 and 5.21.

Chemical-bonds analysis was performed using an FTIR Nicolet 210 spectrophotometer, operated in the range of 400–4000 cm^{-1}, with a 4 cm^{-1} resolution. The refractive index of the films was measured ex situ by ellipsometric measurements, by means of a null single wavelength (632.8 nm) Gaertner L117 ellipsometer.

The atomic profiles of the silicon nitride films were measured using two particle accelerators. A Van de Graaff tandem accelerator (HVECO EN model) located in the Instituto Nacional de Investigaciones Nucleares equipped with a SNICS II ion source generated a 10.0 MeV $^{12}C^{3+}$ beam that has been used for the EFA [9] technique to deduce the $Si_xN_yH_z$/Si films stoichiometry. The incident beam bombarded the samples at an angle 60° relative to the target surface normal and the surface barrier detector scattering angle was set at 45°. The $^{12}C^{3+}$ ions elastically scattered by the Si and N nuclei in a forward direction and the hydrogen recoil nuclei were measured in the same spectra with a good mass resolution.

A single ended 5.5 Van de Graaff (HVECO CN model) located at the Universidad Nacional Autonoma de Mexico produced a 0.825 MeV $^{2}H^{+}$ beam. RBS/NRA methods were applied in order to measure the O and C concentrations in the films. In this case, the targets were positioned normal to the incoming beam and the surface barrier detector was set at an angle of 150°.

3. Results and discussion

Fig. 1, shows a typical EFA experimental spectrum (dots) for the 10.0 MeV $^{12}C^{3+}$ beam on a silicon nitride film corresponding to a production parameter $R = 1.75$. The solid line represents the SIMNRA [10] simulation to fit the spectrum. The simulation of each of the 6 analyzed films, was done with three sublayers: (a) the surface sublayer, which provides the film $Si_xN_yH_z$ stoichiometry and thickness, (b) the interfacial sublayer, which provides the SiH_x composition and thickness, and (c) the silicon substrate. Table 1 summarizes the fitting parameters of each SiN spectrum. Stoichiometry parameters x:y:z of the Si_x:N_y:H_z film are determined for the homogeneous region of the film, away from the interface and surface. The total thickness of a particular element is given as atoms/cm^2, which includes both the interface and surface region. The corresponding standard errors are given in parenthesis as the error in the last digits.

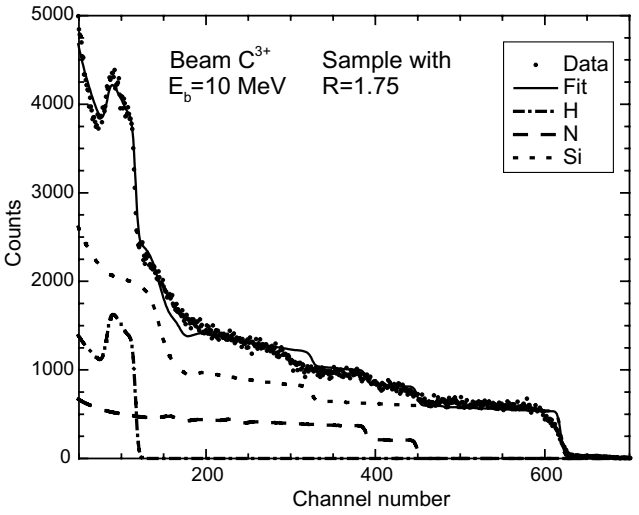

Fig. 1. A typical elastic forward scattering experimental spectrum (dots) for the 10.0 MeV $^{12}C^{3+}$ beam bombardment of a film. The solid line is a SIMNRA fit to the spectrum. The individual contributions of the elastically scattered C ions by Si and by N nuclei, as well as the hydrogen recoil events, are also shown.

Fig. 2, shows the experimental spectrum (dots) produced by a 0.825 MeV $^{2}H^{+}$ beam bombardment of the same silicon nitride film shown in Fig. 1. NR peaks identified were: $^{16}O(d,p_1)^{17}O$ and $^{12}C(d,p_0)^{13}C$, $^{14}N(d,p_i)^{15}N$ [$i = 5,4,3$, and 1–2] and $^{14}N(d,\alpha_1)^{12}C$. The inset figure is the RBS low energy region. The solid line represents the SIMNRA simulation using only one front layer with SiN_x composition and the Si substrate. The $^{16}O(d,p_1)^{17}O$ and $^{12}C(d,p_0)^{13}C$ NR cross sections from www.nds.iaea.org/ibandl were used to obtain the O and C concentrations of the films, which are also summarized in Table 1.

The refractive indexes of the films are also shown in Table 1 and they are in the range from 1.4 to 2.3. As expected, the highest refractive index corresponds to the film with the highest relative content of silicon, and the film with the lowest silicon content has the lowest refractive index.

Typical fourier transform infrared (FTIR) transmission spectra of films deposited under different $R = NH_3/SiH_4$ flow rates are shown in Fig. 3. A broad and intense absorption band centered around 860 cm^{-1}, and a small peak

Table 1
A summary of the EFA and NRA fit parameters for the six samples

Gas flow ratio NH_3/SiH_4	Film stoichiometry $Si_x:N_y:H_z$ $x+y+z=1$			Total concentrations				Refractive index n
				Constituents (10^{18} at/cm^2)		Contaminants (10^{15} at/cm^2)		
	Si	N	H	N	H	O	C	
1.75	0.31 (3)	0.42 (4)	0.27 (2)	2.83 (26)	1.83 (16)	9	9	1.40
2.35	0.33 (3)	0.41 (4)	0.26 (2)	3.24 (29)	2.05 (18)	24	24	1.50
2.91	0.29 (2)	0.43 (4)	0.28 (2)	2.83 (25)	1.84 (17)	12	16	1.80
3.45	0.28 (2)	0.40 (4)	0.32 (3)	2.37 (26)	1.24 (14)	8	20	1.60
3.92	0.27 (2)	0.41 (4)	0.32 (3)	2.39 (21)	1.86 (17)	8	16	1.90
5.21	0.30 (3)	0.39 (3)	0.31 (3)	4.29 (70)	3.41 (31)	8	16	2.30

Stoichiometry parameters $x:y:z$ of the $Si_x:N_y:H_z$ film were taken for the homogeneous region of the film, away from the interface and surface. Total thickness of a particular element is given in atoms/cm^2 units. Standard errors are given in parenthesis as the mean error in the last digits. The refractive indexes shown were obtained by ellipsometric measurement.

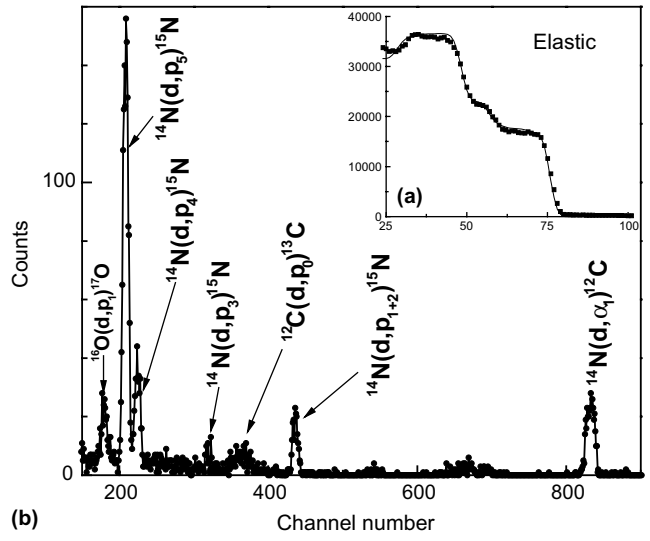

Fig. 2. The experimental spectrum (dots) produced by a 0.825 MeV $^2H^+$ beam bombardment of the same film as in Fig. 1, (a) the RBS low energy region (inset figure) and (b) NR high energy region that corresponds to the indicated NR peaks produced by the $^2H^+$ bombardment on C, O and N nuclei.

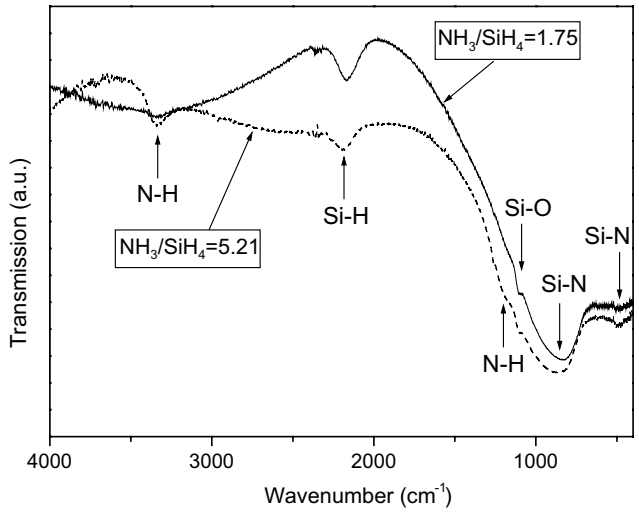

Fig. 3. Typical FTIR spectra of hydrogenated silicon nitride films deposited by PECVD using different values of the flow rate (R).

around 475 cm^{-1} clearly appear in all spectra. They are associated to the asymmetric stretching of Si–N bonds and Si breathing vibrations in silicon nitride films, respectively [11,12]. The absorption peaks, at 3335 cm^{-1} and 1175 cm^{-1} are related to the stretching and bending vibrations of N–H bonds, respectively, and that located at 2185 cm^{-1} is related to the Si–H bonds [13]. The small absorption peak located at 1085 cm^{-1} can be associated to Si–O–Si bonds [13]. As can be clearly appreciated by comparison of the spectra in Fig. 3, the intensity of the main absorption band related to the N–H bonds (3335 cm^{-1}) is lower for the film deposited with $NH_3/SiH_4 = 1.75$ (dashed spectrum) than that for the film deposited with $NH_3/SiH_4 = 5.21$ flow rates (solid spectrum), and the opposite happens with the intensity of the band related to the Si–H bonds (2185 cm^{-1}). Since the intensity of these bands is proportional to the amount of the corresponding bonds, these results indicate that the total amount of hydrogen incorporated in the films, in the form of Si–H and N–H bonds, is approximately constant, which is quite consistent with the IBA results.

4. Conclusions

The IBA results show that the hydrogen concentration in the PECVD silicon nitride films is almost constant (see Table 1), with values about 27 at.% for values of the parameter R between 1.75 and 2.91, and that this concentration increases slightly (about 31%) for $R \geqslant 3.45$. The origin of the low O and C concentrations found in the films could be the out gassing of water and hydrocarbon molecules adsorbed on the walls of the reactor chamber, although the oxygen incorporated can also be due to post-deposition oxidation of the films.

In our experimental EFA set-up, the cross section for the kinematically reversed recoil process $^1H(^{12}C,p)^{12}C$

corresponds to $^{12}C(p,p)^{12}C$, for a proton energy of 0.84 MeV and an angle of 85.2°. A search in the www.nds.iaea.org/ibandl compilation shows that the cross sections for this energy are well described by Rutherford cross sections. Also, with EFA it was possible to simultaneously measure the contributions from nitrogen and silicon. The contaminations of oxygen and carbon were not adequately determined from these spectra. Therefore a RBS/NRA method was used to determine these contaminants.

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