

Quantitative Auger depth profiling of LPCVD and PECVD silicon nitride films

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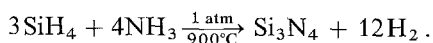
Quantitative Auger-Tiefenprofilanalyse von LPCVD- und PECVD-Siliciumnitridfilmen

Summary. Thin silicon nitride films (100–210 nm) with refractive indices varying from 1.90 to 2.10 were deposited on silicon substrates by low pressure chemical vapour deposition (LPCVD) and plasma enhanced chemical vapour deposition (PECVD). Rutherford backscattering spectrometry (RBS), ellipsometry, surface profiling measurements and Auger electron spectroscopy (AES) in combination with Ar⁺ sputtering were used to characterize these films. We have found that the use of (p-p)heights of the Si LVV and N KLL Auger transitions in the first derivative of the energy distribution (dN(E)/dE) leads to an accurate determination of the silicon nitride composition in Auger depth profiles over a wide range of atomic Si/N ratios. Moreover, we have shown that the Si KLL Auger transition, generally considered to be a better probe than the low energy Si LVV Auger transition in determining the chemical composition of silicon nitride layers, leads to deviating results.

1 Introduction

The growth of silicon nitride films by Low Pressure Chemical Vapour Deposition (LPCVD) and Plasma Enhanced Chemical Vapour Deposition (PECVD) has attracted a great attention in the field of microelectronics during the last years.

LPCVD is a process in which two types of gases react at about one atmosphere and at high temperature to form a solid and a gas phase. Using ammonia (NH₃) and silane (SiH₄) as reactants, the formation of silicon nitride (Si₃N₄) occurs according to:



PECVD is also a gas phase reaction leading to a solid silicon nitride film on a substrate, the reaction temperature, however, being significantly lower, i.e. about 300°C. In PECVD, the chemical reactions are promoted by a glow discharge. The high energy electrons which constitute the discharge ionize and dissociate the gaseous molecules resulting in chemically active radicals and ions. The major

advantage of PECVD over LPCVD is the fact that thermal energy is not needed in order to induce the chemical reactions, thus making PECVD an ideal method to deposit materials on temperature sensitive substrates like polymers and metals having a low melting point.

Silicon nitride layers obtained by PECVD are used mainly in integrated circuits for final passivation because of their impermeability to mobile ions, their hardness (scratch resistance) and low temperature processing, allowing deposition after aluminium metallization. The film composition critically depends on the deposition parameters like gas pressure, gas phase composition, rf frequency, power, and temperature. The quality of the silicon nitride film can be directly related to the atomic composition. Therefore, it is crucial to have a reliable technique which can determine the atomic composition of such films.

The characterization of these films requires a complex study and the techniques used by a number of authors to determine the chemical composition is questionable. Auger electron spectroscopy (AES) combined with Ar⁺ sputter profiling is often used to determine the compositional uniformity of the silicon nitride film as a function of depth. Important work with respect to the quantitative aspects of an Auger in-depth analysis has been performed by van Oostrom and co-workers [1]. A quantitative analysis with an accuracy of ≈ 10% could be made. A disadvantage of their method is that an extensive calibration of the Auger spectrometer is needed. By combining AES and electron energy loss spectroscopy (EELS) Lieske and Hezel [2] were able to provide quantitative information about the chemical composition in thin amorphous silicon nitride layers. They used the peak-to-peak (p-p) heights of the Si KLL and N KLL Auger transitions in the first derivative (dN(E)/dE) of the energy distribution to obtain the atomic ratio of the silicon to nitrogen concentration, Si/N. It has been argued that the high energy Si KLL Auger peak is a better probe than the stronger and easier obtainable Si LVV Auger peak [1–5], since the Si KLL Auger lineshape is less influenced by the surface chemistry. However, many authors have used the Auger (p-p) ratio Si(LVV)/N(KLL) as an indicator of silicon nitride composition [3,6,7–11]. A number of them used this ratio even without a Si₃N₄ standard [7, 12, 13] which, to our opinion, may lead to erroneous results.

The aim of this paper is to demonstrate that the Si(LVV)/N(KLL) Auger (p-p) ratio is a reliable indicator of the silicon nitride composition in Auger depth profiles over a

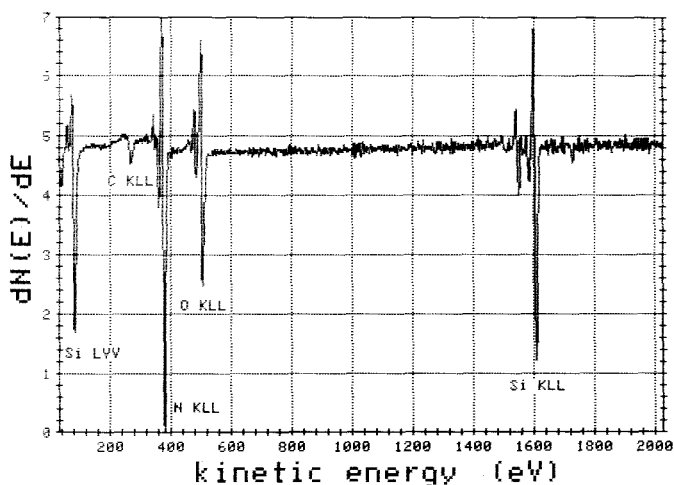


Fig. 1. Auger spectrum of an LPCVD silicon nitride (sample LPCVD in Table 1) at the surface region before Ar^+ sputtering

wide range of Si/N ratios. For that purpose 4 thin silicon nitride films (1 prepared by LPCVD and the other 3 by means of PECVD and a $\langle 100 \rangle$ oriented silicon substrate) with atomic Si/N ratios ranging from 0.68 to 0.95 [as measured by Rutherford Backscattering Spectrometry (RBS)] were investigated.

2 Experimental

The LPCVD silicon nitride films were grown on 2 and 4 inch silicon wafers (p-type, (100) orientation, $10 \Omega\text{cm}$). The wafers were cleaned prior to the deposition with a standard procedure including a dip in a 1% HF solution in order to remove the native oxide. The deposition conditions were: a $\text{SiH}_2\text{Cl}_2/\text{NH}_3$ gas mixture, temperature (T) of 800°C , total pressure (P) of 25 Pa and a growth rate of 5.0 nm/min.

The PECVD silicon nitride films were prepared in a TEMPRESS hot-wall reactor (OMEGA-5000) under the following conditions: a SiH_4/NH_3 gas mixture, $T = 300^\circ\text{C}$, $P = 133$ Pa, deposition rate of 30.0 nm/min. Both silicon and nitrogen rich layers were prepared by varying the SiH_4/NH_3 ratio.

The refractive index is also a good indicator of the ratio Si/N. A refractive index $n = 2.0$, however, does not necessarily mean stoichiometric Si_3N_4 as shown by Allaert et al. [13]. The refractive index was measured by ellipsometry (wavelength incident laserbeam = 632.8 nm, angle of incidence = 70°). Step measurements with a surface profiler (DEKTAK) and ellipsometry were applied to determine the silicon nitride film thickness with high accuracy.

The RBS analyses were performed on each sample presented in this paper, using a 2 MeV He beam with a cross sectional area of approximately 1 mm^2 at a working pressure of about 1×10^{-6} Torr. The backscattered alpha particles were counted by a solid state detector (energy resolution: 15 keV).

For the analysis of the silicon nitride layers we used a PHI 600 SAM (scanning Auger microscope) system with facilities for scanning electron microscopy (SEM), the achieved lateral resolution being 19 nm, and Ar^+ depth profiling.

In the PHI 600 system the primary beam (beam energy = 10 keV, beam current = 500 nA, beam diameter = 0.7 μm ,

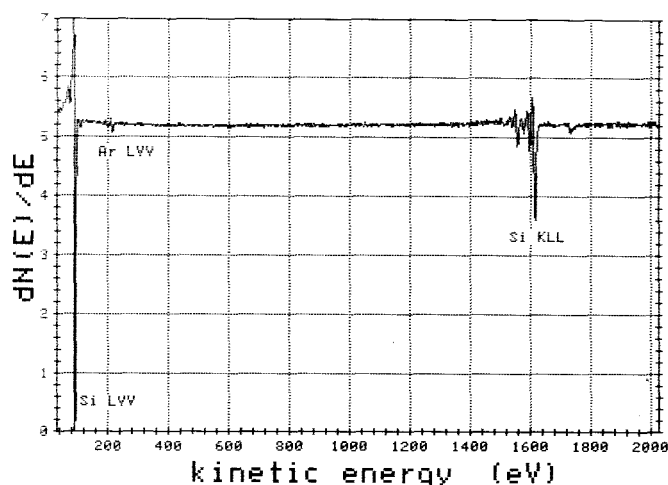


Fig. 2. Auger spectrum of the silicon substrate after removal of the LPCVD silicon nitride layer by argon ion sputtering

angle of incidence with the surface normal = 30°) was rastered over a surface area of $400 \mu\text{m}^2$. Under these conditions possible electron beam induced effects (desorption, dissociation) were not observed. The resolution of the cylindrical mirror analyser was set at 0.6%.

The differentially pumped ion gun was adjusted to produce an argon ion beam with an ion energy of 3.5 keV and a FWHM of 200 μm . The angle of incidence with the sample surface was 45° and the ion beam was rastered to produce a crater of $2 \times 2 \text{ mm}^2$. The sputter rate of silicon nitride was calibrated and found to be 5.7 nm/min. Calibration was performed on an LPCVD layer of thickness, d , 106.0 nm (sample LPCVD in Table 1), as independently established from ellipsometry, surface profiling (DEKTAK), and RBS. Alternate sputtering and Auger analysis were used during an in-depth analysis.

3 Results and discussion

Figure 1 shows the Auger spectrum of the LPCVD silicon nitride surface region. It reveals oxygen and a small amount of carbon in addition to nitrogen and silicon (the low energy Si LVV (Si 1) and high energy Si KLL (Si 2) Auger peaks). The small amount of surface oxygen (see Fig. 1) present on all four samples investigated, arises from a slight post-growth oxidation of the nitride in air [14]. Carbon surface contamination is a phenomenon which is usually observed with samples which have been exposed to air. The thickness of the C layer was found to be less than 5 \AA on all nitride films investigated.

Displayed in Fig. 2 is the Auger spectrum after complete removal of the nitride film. The spectrum now only shows free silicon and a small amount of implanted argon.

The measured Auger in-depth profile of a 106 nm LPCVD silicon nitride film, considered as a reference sample, is shown in Fig. 3. The (p-p) heights of the Si LVV (Si 1), Si KLL (Si 2), N KLL (N 1) and O KLL (O 1) Auger peaks in the $dN(E)/dE$ mode have been plotted as a function of sputter time. The small oxygen signal near the interface between the nitride and the silicon substrate is due to re-growth of a thin silicon oxide layer after the HF dip (see section 2). In the silicon nitride itself the oxygen concentration is below the detection level of 0.1%. From RBS it

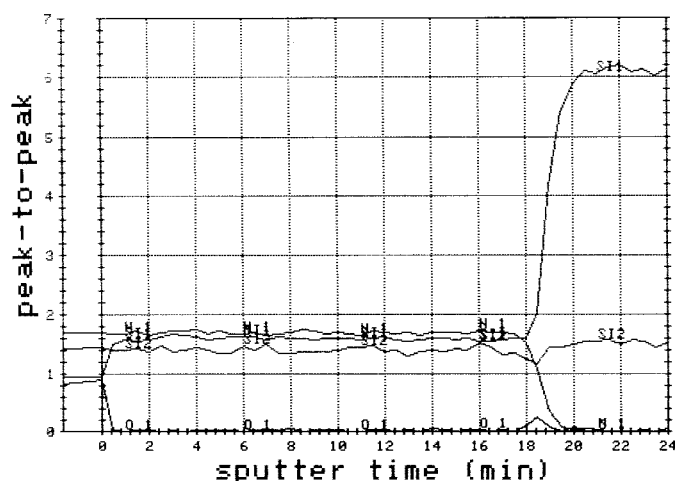


Fig. 3. AES in-depth profile of an LPCVD silicon nitride film (sample LPCVD in Table 1). The Auger peak-to-peak heights of the Si LVV (Si 1), Si KLL (Si 2), N KLL (N 1) and O KLL (O 1) peaks in the $dN(E)/dE$ mode are plotted as a function of sputter time

was established that the atomic Si/N ratio of this sample (LPCVD in Table 1) is 0.75 (experimental error $\leq 2\%$). The quantitative elemental composition from the measured Auger in-depth profile (Fig. 3) was deduced using either the Si LVV or Si KLL (p-p) heights following a relation extensively discussed in the literature [5, 15]. Using the Si LVV Auger (p-p) height (Si 1) the relative sensitivity factor (rsf) for Si 1 had to be changed from 0.15 [15] to 0.203 in order to obtain 0.75 for the atomic Si/N ratio (for N1 and O1 the handbook rsf values were used [15]). Use of Si 2 rsf (Si 2) had to be increased to 0.179, this value being almost 4.5 times larger than the handbook value of Si KLL in elemental silicon [15]. This large deviation in rsf (Si 2) may be due to more complex factors than proposed by van Oostrom et al. [1]. A detailed study of this matter is in progress.

The elemental composition of the three PECVD silicon nitride layers (see Table 1) was derived using the rsf (Si 1, Si 2) values as determined from the Auger in-depth profile of the LPCVD sample, i.e., rsf (Si 1) = 0.203 and rsf (Si 2) = 0.179. All three PECVD films were found to be homogeneous [16].

Table 1 summarizes the most important results. The first column of Table 1 shows the way the film is grown, the second shows the refractive index n , the third shows the thickness d of the silicon nitride film, the fourth contains the atomic Si/N ratio as determined by RBS, the fifth and sixth display the atomic Si/N ratio as derived from the Si LVV- and Si KLL (p-p) heights, respectively, using the modified rsf values. From Table 1 it can be seen that agreement between RBS and AES (using Si LVV) results is striking. Atomic Si/N ratios as derived using Si KLL (sixth column) show a much larger deviation from the RBS values (fourth column). This deviation may be ascribed to (strong) matrix effects of the high energy Si KLL Auger electrons, as proposed earlier by Garner et al. [17].

4 Conclusions

We have shown that an accurate chemical composition, in terms of atomic Si/N ratio, can be deduced from the peak-

Table 1. Summary of the results showing the refractive index n , the thickness of the silicon nitride layer d , the atomic Si/N ratio as measured by RBS and the ratio derived from the Auger in-depth profiles

Sample	n	d (nm)	Si/N		
			RBS	Si LVV	Si KLL
LPCVD	2.00	106	0.75	0.75	0.75
PECVD1	1.91	115	0.67	0.66	0.71
PECVD2	2.09	130	0.95	0.92	0.81
PECVD3	1.98	210	0.68	0.66	0.72

to-peak heights of the Si LVV and N KLL Auger transitions in the first derivative of the energy distribution, $dN(E)/dE$, over a rather wide range of Si/N ratios.

As the Si KLL Auger lineshape is less sensitive to the chemical environment than the Si LVV Auger lineshape [1, 5], its use in Auger in-depth profiles to determine the chemical composition of silicon nitride layers leads to less accurate results.

The reference silicon nitride sample does not need to be stoichiometric Si_3N_4 . Once the elemental composition of the reference sample has been determined by RBS, the relevant relative sensitivity factors (for Si LVV or Si KLL) can be adjusted in a very simple way to yield the RBS atomic Si/N ratio. This procedure is valid for silicon nitride samples with significant variation in chemical composition relative to the reference sample.

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