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ANALYSIS OF SILICON NITRIDE LAYERS DEPOSITED FROM SiH_4 AND N_2 ON SILICON

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Abstract—Backscattering and channeling effect measurements of 1 MeV $^4He^+$ ions were used to determine the composition and density of Si_xN_y layers on single crystal silicon. The nitride layers were deposited by the reaction between SiH_4 and N_2 in a glow discharge at 350°C. The ratio N/Si in the layer decreases with increasing SiH_4 concentration and total pressure of the reaction gases whereas the density is nearly constant. Conditions for deposition of stoichiometric nitride layers were optimized. These results are in good agreement with measurements of etching rate and index of refraction. The composition of all samples is homogeneous over the entire layer.

1. INTRODUCTION

THIN films of silicon nitride are of interest in semiconductor device technology. In contrast to silicon dioxide layers they show little ion drift and good sealing properties. The standard method for the production of nitride layers is the chemical vapor deposition using the silane–ammonia reaction at temperatures above 700°C. Recently a new method was reported[1, 2] which starts from SiH_4 and N_2 and yields perfect nitride layers. The low deposition temperature (350°C) and the absence of ammonia, which always contains water and alkali ions, is very convenient for planar device passivation.

The object of this investigation is the structure of nitride layers from SiH_4 and N_2. The energy analysis of backscattered ions allows one to identify the mass of the target atoms and to select a certain depth in the amorphous layer and in the Si substrate simply by evaluating corresponding portions of the energy spectrum. Furthermore backscattering of MeV $^4He^+$ ions can be used to determine the concentrations and distributions of nitrogen and silicon in the layers. By alignment of the incident beam direction with a crystal axis of the silicon substrate the yield of backscattered particles is reduced (channeling effect) and a more accurate determination of the nitrogen concentration can be made. These techniques have been used to analyse silicon dioxide layers[3] and nitride layers from SiH_4 and NH_3[4, 5]. For comparison with the backscattering data in this work, other structure dependent measurements as etching rate and index of refraction have been performed.

2. EXPERIMENTAL

The nitride layers were deposited on 500 Ω cm, ⟨111⟩-oriented, boron-doped silicon wafers. Prior to deposition the surfaces were mechanically and chemically polished and thoroughly cleaned using conventional methods. Figure 1 shows the nitride deposition apparatus. The reaction between SiH_4 and N_2 takes place in a r.f. discharge inside of a quartz tube. The discharge is activated by a coil or a capacitor located outside the tube. The r.f. generator is operated at a frequency of 500 kHz. The wafer susceptor made from quartz contains a resistance heater. For purity and control purposes the whole gas flowing system satisfies high vacua requirements.

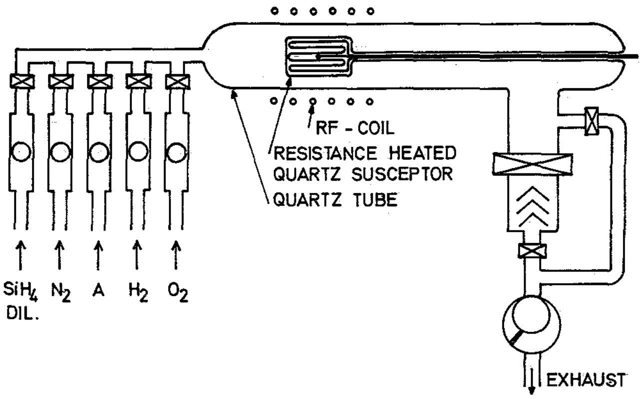

Fig. 1. Schematic drawing of the nitride deposition apparatus.

SiH_4 is used in a 2 per cent dilution in N_2. The ratio SiH_4/N_2 in the reaction chamber can be varied from 10^{-4} to $1 \,.\, 10^{-2}$ by mixing the SiH_4 gas with a separate N_2 stream. The gases N_2, Ar, H_2 and O_2 can be used for glow discharge cleaning steps just prior to the deposition process.

The backscattering and channeling apparatus is illustrated in Fig. 2. In this work 1 MeV $^4He^+$ ions are used. The samples are mounted on a two axis goniometer to permit the alignment of the beam with one of the crystal axes of the silicon substrate. The beam current is measured with an integrator; the target is shielded with a Faraday cup to avoid errors by secondary electron emission. The energy distribution of the backscattered $^4He^+$ ions is measured with a surface barrier detector.

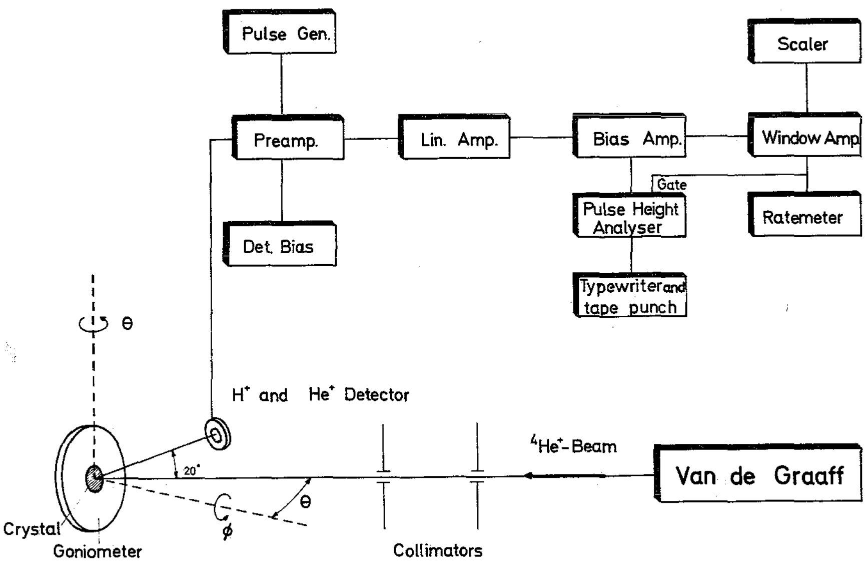

Fig. 2. Schematic illustration of the experimental arrangement in the target chamber together with the electronic instrumentation for energy analysis of backscattered particles.

The electrical signal from this detector is amplified and stored in a pulse height analyzer. The linear response of the nuclear particle detector provides a fixed energy per channel in the multichannel analyzer. The system conversion gain is 1·48 keV per channel. The energy resolution of the detecting system is about 10 keV, this corresponds to a depth resolution in the silicon nitride layer of about 150 Å for the beam energy and experimental geometry used.

3. ANALYSIS

A detailed description of the analysis technique has been given elsewhere[3]. For convenience the most important features of the analysis are summarized. In Fig. 3 random (cross-bars) and oriented (black dots) spectra are shown for illustration. Three portions of the spectra clearly can be identified. The first part for channel numbers greater than 190 is produced by $^4He^+$ particles backscattered from silicon atoms in the nitride layer. In the energy range called HW_N and the corresponding peak area HW_N times R_N, particles are backscattered from nitrogen atoms in the nitride layer. All other counts in the channel range from 0 to 190 are produced by $^4He^+$ ions, backscattered from silicon atoms in the substrate. The height of the step, R_{Si}, (number of counts in one channel) is proportional to the concentration of silicon atoms in the nitride layer and the width of the step ΔE is proportional to the layer thickness. In the random spectra R'_{Si} is proportional to the concentration of silicon atoms in the substrate. If the incident beam is aligned with a crystal axis, the contribution from the substrate is strongly reduced and permits a more accurate determination of the nitrogen concentration. The net height of the nitrogen peak, R_N, is proportional to the concentration of the nitrogen atoms and the width of the peak, HW_N, is proportional to the layer thickness. The proportionality constant is $[S]$, the backscattering energy loss parameter. The energy scale in Fig. 3 can be converted in a depth scale, t, by $\delta E = \delta t[S]$ where $[S] = \alpha \,.\, dE/dx|_{E_0} + \cos\theta_L^{-1}.\, dE/dx|_{\alpha E_0}$; α is the fractional amount of the energy after scattering and dE/dx is the specific energy loss at E_0 and αE_0, the energy before and after scattering respectively.

The concentration ratio of nitrogen to silicon $N_N(t)/N_{Si}(t)$ at depth t in the layer is given by

$$\frac{N_N(t)}{N_{Si}(t)} = \frac{R_N(E)\,[S_N]}{R_{Si}(E)\,[S_{Si}]}\,\frac{\sigma_{Si}}{\sigma_N} \quad (1)$$

where σ is the scattering cross section in the laboratory system, $\sigma_{Si}/\sigma_N = 4{\cdot}3$ in our experi-

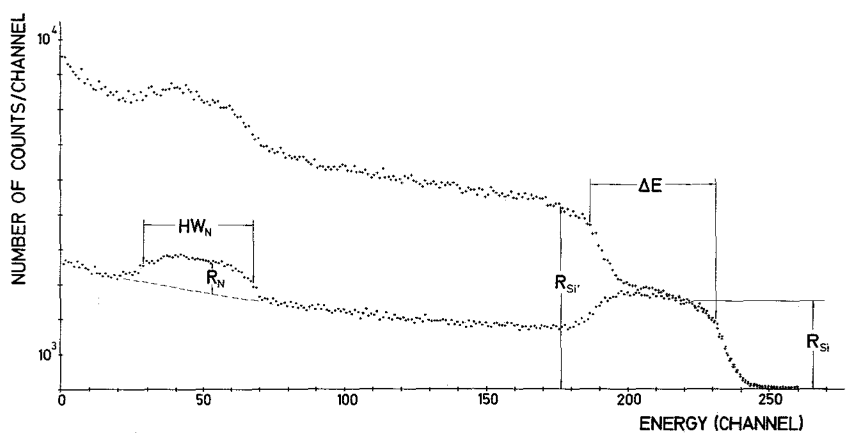

Fig. 3. Random and aligned spectra for 1 MeV $^4He^+$ ions scattered from a 953 Å silicon nitride layer deposited on 111 oriented silicon.

mental arrangement. The ratio $[S_N]/[S_{Si}]$ can be determined by the measured ratio $HW_N/\Delta E$. If the layer thickness is known from ellipsometry measurements, an absolute depth scale can be determined.

The values of N_{Si} can be calculated by comparing the silicon concentration in the nitride layer, N_{Si}, to that of silicon, N'_{Si}, in the substrate

$$N_{Si} = N'_{Si} \frac{R'_{Si}[S'_{Si}]}{R_{Si}[S_{Si}]} \quad (2)$$

$[S'_{Si}]$ can be calculated from values of the specific energy loss in silicon[6]. N_N can then be determined by equation (1).

The density ρ of the layer can be expressed by

$$\rho = \frac{N_{Si}}{L}\left[M_{Si} + \left(\frac{N_N}{N_{Si}}\right) M_N\right] \quad (3)$$

where L is Avogadro's number and M the atomic weight.

4. RESULTS

In a first series of layers the influence of SiH_4 concentration on the composition was studied. The SiH_4 concentration was varied from $2 \cdot 10^{-2}$ per cent to 2 per cent. The total pressure during deposition was kept constant, the temperature of the substrate was always 350°C. The results of the analysis are presented in Fig. 4. The ratio N_N/N_{Si} was determined by equation (1) as an average over the layer thickness. With increasing SiH_4 concentration the ratio N_N/N_{Si} decreases. The dependence can be described by $N_N/N_{Si} = 1{\cdot}06 - 0{\cdot}143 \ln x$ where x is the SiH_4 concentration in per cent. The composition is found to be stoichiometric in the range of $0{\cdot}1 \leq x \leq 0{\cdot}2$. Results given in[5] for nitride layers from SiH_4 and NH_3 show, that with increasing NH_3/SiH_4 gas ratio the composition became stoichiometric as an saturation level. With the glow discharge method however it is possible to further increase the N_N/N_{Si}-ratio. The composition can be made silicon-rich or nitrogen-rich. This is supported by the results of etching rate measurements, also presented in Fig. 4. The etching rate reaches a maximum just in the SiH_4 concentration region, where the composition is stoichiometric. Again this is in contrast to measurements in[5] where the etching rate goes to an upper saturation level for stoichiometric layers. Index of refraction

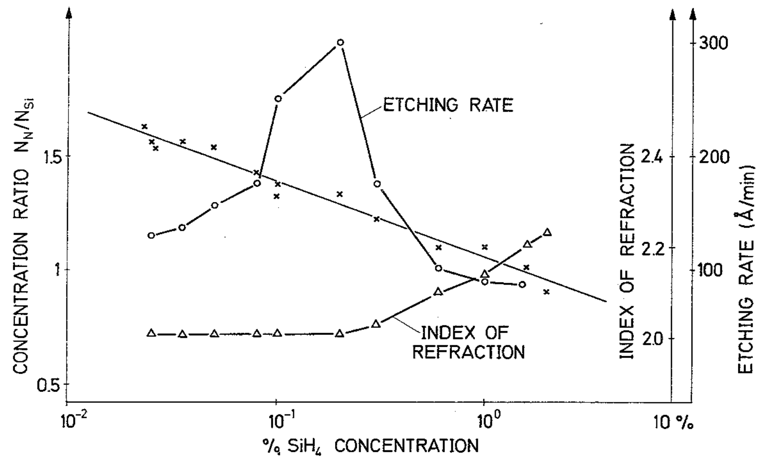

Fig. 4. Concentration ratio of nitrogen to silicon atoms as a function of the SiH_4 concentration in the deposition apparatus. Included are corresponding curves of etching rate and index of refraction.

measurements, which are also included in Fig. 4 substantiated the given results. For SiH_4 concentrations below 0·2 per cent where the composition changes from stoichiometric to nitrogen-rich $n = 2{\cdot}01$ and independent of the SiH_4 concentration. Above 0·2 per cent n increases.

The distribution of the N_N/N_{Si} ratio over the layer thickness with the SiH_4 concentration as a parameter is presented in Fig. 5. The results show that the composition is homogeneous over the total range of SiH_4 concentration used during the fabrication of the nitride layers. Deviations at the surface or at the interfaces (see Fig. 5) may be caused by uncertainties in the determination of the corresponding depth at the edges of the nitrogen and the silicon peak.

In Fig. 6 the average concentrations of silicon and nitrogen atoms in the silicon nitride

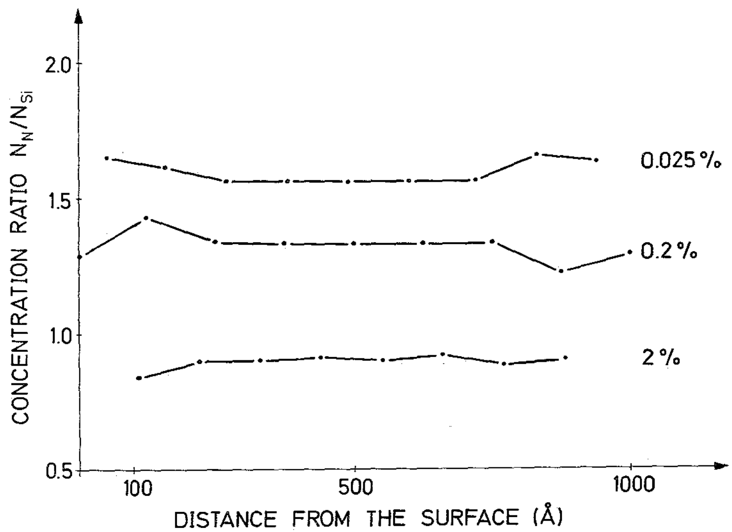

Fig. 5. Distribution of N_N/N_{Si} for samples prepared with different SiH_4 concentrations.

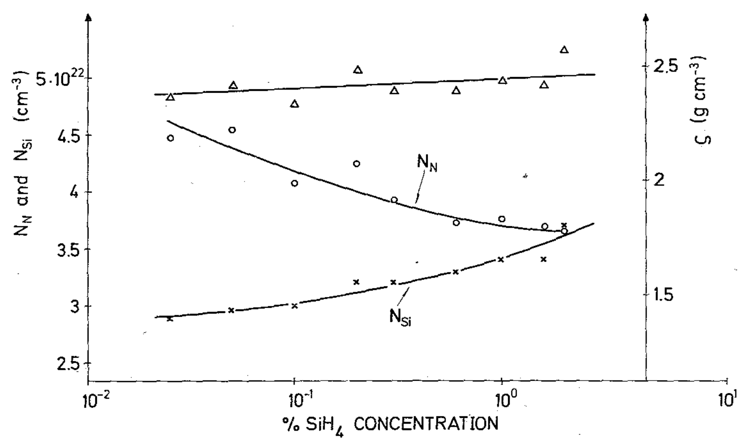

Fig. 6. Average atomic concentrations and densities of silicon nitride layers as a function of the SiH_4 concentration during deposition.

layers are shown in dependence of the SiH_4 concentration. N_{Si} was calculated using equation (2), $[S'_{Si}]$-values were determined using dE/dx-values for 1 and 0·58 MeV $^4He^+$ ions in silicon given in [6]; the estimated error is about 10 per cent. $[S_{Si}]$-values were determined from measured ΔE values together with layer thickness data, found by ellipsometry measurements. The average $[S_{Si}]$ value obtained was 67 eV/Å for 1 MeV $^4He^+$ ions. The results in Fig. 6 show a slight increase for N_{Si} from 3 to $3{\cdot}7 \,.\, 10^{22}/cm^3$ with increasing SiH_4 concentration. Within the estimated total error of 15 per cent N_{Si} may be considered as constant for SiH_4 concentrations below 0·2 per cent. N_N however decreases from 4·5 to $3{\cdot}6 \,.\, 10^{22}/cm^3$ with increasing SiH_4 concentration. The average density of the silicon nitride layer, calculated by equation (3) is also presented in Fig. 6. The density is nearly independent of the SiH_4 concentration with an absolute value of about 2·5 g cm^{-3}; of course a systematic error of about 10 per cent cannot be excluded.

Among other fabrication parameters that can be varied in the glow discharge deposition method the total pressure during deposition seems to have a strong influence on the composition. To study this influence the total pressure was varied between 0·25 and 2·8 Torr, the SiH_4 concentration was kept constant at 0·08 per cent. The results of the analysis are given in Fig. 7. N_N/N_{Si} ratio decreases with increasing pressure but within the pressure region between 1 and 2 Torr the dependence is very weak. Again this result is supported by index of refraction measurements also presented in Fig. 7. For the SiH_4 concentration of 0·08 per cent n is nearly constant for pressures below 2 Torr while there is a remarkable increase for higher pressures. Quite different behaviour for n was obtained for a SiH_4 concentration of 0·5 per cent, where it is known from Fig. 4 that stoichiometric layers cannot be produced. Here n is above 2 on the whole pressure range besides at 0·2 Torr where a stoichiometric composition can be obtained.

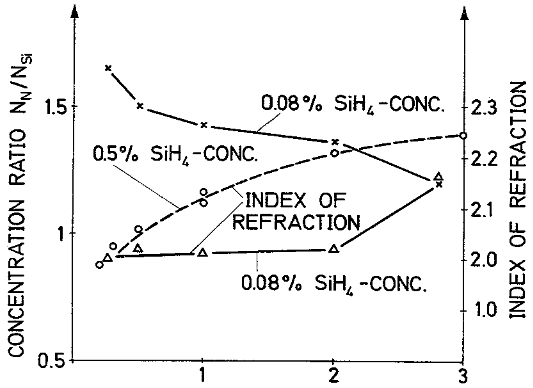

Fig. 7. Concentration ratio of nitrogen to silicon of samples prepared at different total pressures but constant SiH_4 concentration during deposition in the reactor chamber.

5. DISCUSSION

The experimental results show that the composition of nitride layers made from SiH_4 and N_2 depends on the SiH_4 concentration and on the total pressure during deposition. The composition in the layer was found to be stoichiometric for SiH_4 concentrations between 0·1 and 0·2 per cent and in the pressure range from 1 to 2 Torr. In the glow discharge deposition method the N_N/N_{Si} ratio can be varied above and below the stoichiometric value. This was not observed for silicon nitride layers made from SiH_4 and NH_3, where the maximum value obtained for N_N/N_{Si} was 1·33. With increasing SiH_4 concentration N_{Si} increases from 3 to $3{\cdot}7 \,.\, 10^{22}\, cm^{-3}$ whereas N_N decreases from 4 to $3{\cdot}6 \,.\, 10^{22}\, cm^{-3}$. The density of the layer was about 2·5 g cm^{-3} and was found to be nearly independent of the SiH_4 concentration. This is somewhat lower than the values obtained in [5] and less than that of crystalline α–Si_3N_4.

The total pressure is an important parameter in the glow discharge deposition method. For constant SiH_4 concentration of 0·08 per cent stoichiometric compositions are obtained between 1 and 2 Torr. For lower pressures N_N/N_{Si} rises sharply whereas for higher pressures N_N/N_{Si} drops.

The results obtained were in agreement with other methods depending on the structure of the silicon nitride layer. The etching rate, for example, has a sharp maximum for stoichiometric composition whereas the index of refraction became saturated with a value of about 2·01 for N_N/N_{Si} ratios greater 1·3.

One advantage of the backscattering method is the information on depth dependence of the above quantities. The ratio N_N/N_{Si} is independent of depth for all SiH_4 concentrations studied.

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