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ION BEAM INDUCED NITRIDATION OF SILICON

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1. Introduction

High dose ion bombardment of silicon with reactive species, such as oxygen and nitrogen, has attracted considerable interest due to possible applications of beam-induced chemical compounds with silicon [1]. For example, high energy oxygen bombardment of Si is now routinely used to form buried oxide layers for device purposes, the so called SIMOX structures. On the other hand, Si nitrides, formed by low energy (< 1 keV) or high energy (> 100 keV) nitrogen beam bombardment of Si, are attractive as oxidation barriers or gate insulators, primarily due to the low diffusivity of many species in Si nitrides [1]. However, little data exists on silicon nitride formation during bombardment [2,3] and its angle dependence, in particular for N_2^+ bombardment in the 10 keV range, which is of interest for analytical techniques such as SIMS. In SIMS, low energy oxygen ions are more commonly used as bombarding species, as oxygen provides stable ion yields and enhances the positive secondary ion yield. Therefore, a large body of data can be found in the literature on oxide formation during low energy oxygen bombardment [4-7].

Nitrogen bombardment of Si may cause similar effects to oxygen bombardment, as nitrogen and oxygen have similar masses and ranges in Si, show similar sputtering effects and both have the ability to form chemical compounds with Si. In this work we explore this possibility in some detail. We compare oxide and nitride formation during oxygen and nitrogen ion bombardment of Si under similar conditions. Despite the expected similar behaviour, some large differences in compound formation were found.

2. Experimental

In this study we used (100) Si wafers of n-type with resistivity of 10 Ωcm. Oxygen and nitrogen bombardment was carried out either in a Riber MIQ 256 SIMS instrument (in which the primary beam energy and angle of incidence can be changed independently) using 6-12 keV O_2^+ and N_2^+ ions at impact angles from 0°-60° or in an ion implanter using 15-40 keV O^+ and N^+ ions. All samples and SIMS craters, obtained under different conditions (primary beam energy, angle of incidence and the dose of implanted oxygen or nitrogen), were analysed by SIMS (using Cs^+ and O_2^+ beams) and Rutherford backscattering and channeling (RBS-C) (using 2 MeV He^+ ions) to determine the concentration profiles of oxygen and nitrogen and to quantify the influence of primary beam parameters on the formation of surface compounds (oxides and nitrides).

3. Results and discussion

Bombardment of the Si surface with oxygen ions at near-normal incidence eventually transforms the surface into a continuous stoichiometric oxide, SiO_2. Prior to SiO_2 formation, there is a transient region over which the oxygen concentration increases with dose. For typical SIMS conditions, the O^+ build-up profile changes smoothly, with a rather abrupt change at saturation (for high energy primary ions) [8]. The situation is quite different in the case of N_2^+ bombardment, where the build-up profile of N^+ can exhibit several rather intense oscillations before reaching a constant level. This effect is shown in Fig.1a giving the dependence of N^+ buildup profiles on the primary beam angle of incidence. As the impact angle

increases, oscillations become less intensive and at about 30° (measured from the normal to the sample surface) they disappear. This behaviour suggests a critical angle of about 30° below which nitride is formed under the bombardment conditions employed in this study.

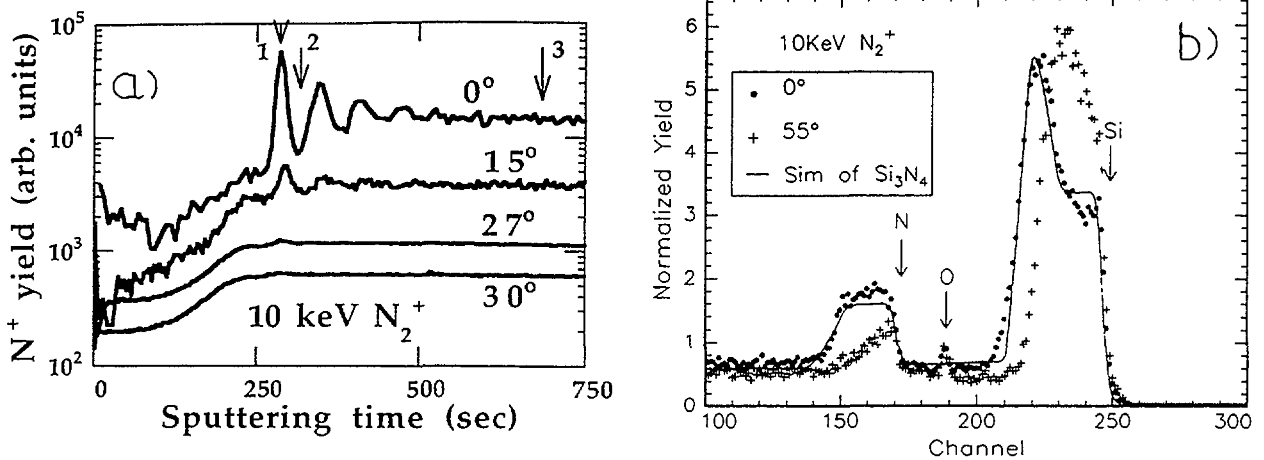

Fig.1: **a)** Build-up profiles of N+, measured during nitrogen bombardment at different impact angles; **b)** RBS-C spectra following 10 keV N_2^+ bombardment of Si during SIMS at two different angles (the solid curve corresponds to RUMP simulation).

To reveal the nitrogen distribution following 10 keV N_2^+ bombardment at different angles of incidence, the craters from Fig.1a were analysed by RBS-C. Fig.1b shows RBS-C spectra for two cases of nitrogen bombardment at 0° and 55° to the surface normal. Bombardment at 0° clearly shows a composition close to Si_3N_4, while the RUMP simulation (solid curve in Fig.1b) indicates substantial over-stoichiometry of the nitride film. In contrast, bombardment at 55° (Fig.1b) does not result in a surface nitride film, but rather in an amorphous Si layer containing high nitrogen content.

The results on angular dependence are summarised in Fig.2a which reveals a pronounced change in nitrogen content at about 30°. For comparison, Fig.2a also shows the angular dependence for oxide formation (normalised to the nitrogen curve), following 10 keV

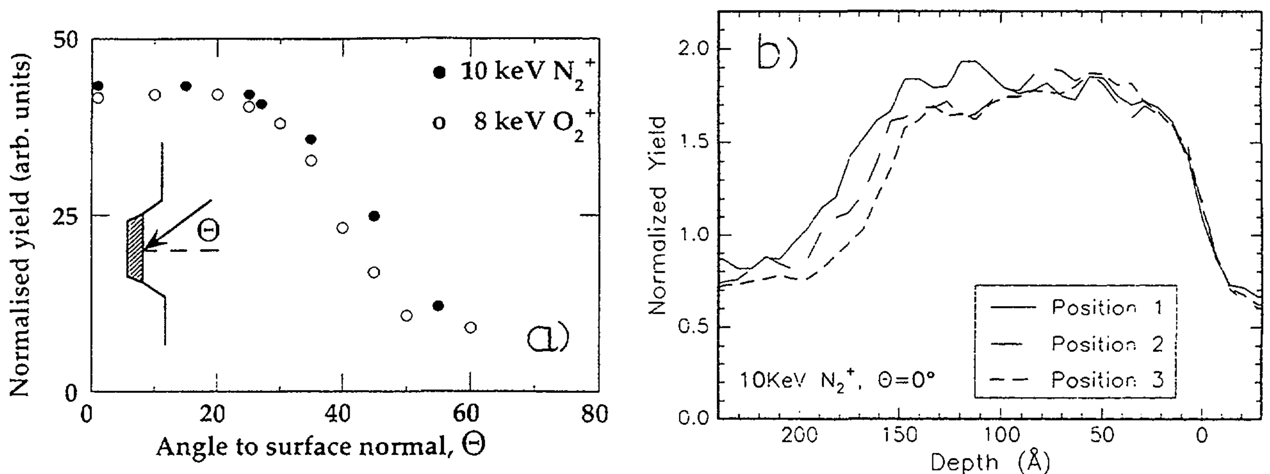

Fig.2: **a)** Normalised angular dependencies of oxide and nitride formation; **b)** RBS-C nitrogen profiles collected from within SIMS craters labelled with 1, 2 and 3 in Fig.1b.

O_2^+ bombardment. As expected from similar ranges and sputtering rates in Si, both oxygen and nitrogen bombardment exhibit similar angular dependence of compound formation.

To explain the differences between oxygen and nitrogen bombardment, one should notice differences in formation and properties between Si and its oxide and nitride. There is a large difference in atom density between SiO_2 (7.05E22 atoms/cm^3) and Si_3N_4 (1.03E23 atoms/cm^3). During nitride formation, there is almost no expansion of the Si lattice and this large densification may become more important for compound formation than swelling, which dominates the oxide formation [3]. A consequence of this dramatic densification is a substantial reduction in ion ranges in Si nitride compared with Si, R_p=96Å and 150Å, respectively for 5 keV N^+ ions from the TRIM'95 code. Another important feature is the low diffusivity of many species, including nitrogen, in Si nitride [2]. On the other hand, the reaction of N to form N_2 is much faster than the reaction of O to form O_2 (due to the stronger N-N bonds than the O-O bonds) and hence high dose nitrogen implantation (with excess nitrogen) may result in formation of N_2 bubbles [1].

Keeping all this in mind, we propose the following explanation for observed differences in oxide and nitride formation and segregation of impurities. The initial stage of buried nitride formation is similar to that of oxide formation: nitrogen is not mobile in disordered Si and the nitrogen concentration below the surface builds up with N dose until a buried nitride layer is formed. With increasing dose, the excess N may be trapped in the Si nitride (low self-diffusion of N in Si nitride and a strong tendency of N to form N_2) contributing to the observed over-stoichiometry of the nitride layer. At the same time the surface is being sputtered away, leading ultimately to the formation of a nitride layer continuous to the surface. Now, the range of N ions in the new Si nitride layer will be drastically reduced contributing again to the over-stoichiometry and leading to reduction in the width of the nitride film as sputtering takes place, consistent with a gradual decrease of film thickness shown in Fig.2b. With increasing dose and sputtering, implanted N again reaches the interface and reacts with Si to increase again the nitride layer thickness above the range of N ions. This process repeats itself until a dynamic equilibrium is reached: sputtering reduces the width of the nitride layer to one comparable to the range (plus straggling) of N in Si nitride. This process may contribute to the SIMS oscillations in N build-up signal, shown in Fig.1a.

In conclusion, we have observed some large differences in the ion beam induced processes of nitridation and oxidation of Si. These differences are explained in terms of quite different atomic diffusivities in oxides and nitrides, film structural differences and thermodynamic properties.

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