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Dynamics of the ion beam induced nitridation of silicon

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High-resolution Rutherford backscattering and channeling has been used to study the energy and angular dependence of the ion beam induced nitridation of Si in a secondary ion mass spectrometry system. The nitridation of Si is characterized by two critical angles θ_{c1} and θ_{c2} , corresponding to the formation of stoichiometric and overstoichiometric Si-nitride layers, respectively. For the N_2^+ bombardment in the 10 to 13.5 keV range, θ_{c1} changes from 40° to 45°, while θ_{c2} changes from 28° to 30°. Further, strong oscillations in the secondary ion signal, observed for angles of incidence below θ_{c2} , are directly related to charging of the Si-nitride surface. We demonstrate that the response of the Si-nitride layer under ion bombardment during the transient stage of nitridation can be described by a second order differential equation. © 2002 American Vacuum Society.

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I. INTRODUCTION

Bombardment of semiconductor surfaces with reactive ions, such as oxygen and nitrogen ions, allows the investigation of the fundamental ion-induced chemical reactions in their near-surface region.^{1,2} Furthermore, the athermal formation of dielectric materials, such as SiO₂ and, especially, Si₃N₄, by ion bombardment has attracted considerable interest as an alternative to the thermal synthesis or the chemical vapor deposition of these materials.² It is worth noting here that the kinetics of thermal nitridation is very slow compared to the oxidation of Si (3×10^{-12} nm s⁻¹ at 1100 °C, compared to ~ 0.3 nm s⁻¹ for oxidation).³ Layers produced by chemical deposition have their structural composition which depends on the deposition parameters, such as deposition pressure, gas flow rates, and substrate temperature.^{4,5} In addition, the electrical properties and thermal stability of plasma-deposited Si-nitride layers are adversely affected by the incorporation of hydrogen, whereas the presence of moisture in plasma-deposited oxides could degrade their dielectric property.⁶

Ion beam oxidation of Si has been used to produce device quality buried oxide layers in silicon-on-insulator structures,^{7,8} while ion beam synthesized nitride layers have been employed as oxidation barriers and gate dielectrics.^{9,10} Furthermore, beams of low-energy oxygen and nitrogen ions are routinely used in secondary ion mass spectrometry (SIMS) for in-depth profiling of impurities in semiconductors. Compound formation in the near-surface region of Si during SIMS analysis with these reactive ions can, however, result in the redistribution of impurities, thus degrading the depth resolution.¹¹⁻¹⁶

The ion beam synthesis of oxides and nitrides of Si involves several, often competing, processes such as simultaneous implantation of ions below the Si surface and sputter removal of the top surface layers. The relative rates of both the buildup of implanted ions and sputtering are determined

primarily by the impact-ion energy and angle of incidence.^{1,2} The formation of shallow buried SiO₂ layers during low-energy ion implantation (<15 keV/oxygen ion) is well documented and explained in the literature.¹⁷⁻¹⁹ Briefly, during oxygen bombardment the implanted oxygen ions remain in disordered Si due to their low mobility in disordered Si and the concentration of oxygen builds up to the threshold level when a buried SiO₂ layer is formed. Oxygen in excess of this threshold level rapidly diffuses out of the SiO₂ layer (high mobility of O in SiO₂) to react with free Si at the Si/SiO₂ interfaces. When the SiO₂ layer recedes to the surface, due to the simultaneous sputtering of the Si surface, the excess oxygen either diffuses out of the sample or reacts with Si at the SiO₂/Si interface. The high mobility of oxygen in oxide ensures that its oxygen content does not exceed the stoichiometric level. The buildup of oxygen to the threshold level required for SiO₂ formation is determined by the penetration depth of implanted oxygen ions and the relative sputtering rate of the Si surface. These parameters depend on the primary ion beam energy and the angle of incidence. The transient stage preceding the formation of a SiO₂ layer continuous to the surface has also been studied.²⁰ We have recently reported the angular and energy dependence of the ion beam oxidation of Si for a wide range of energies.²¹ We have shown that the critical angle of incidence for SiO₂ layer formation increases from $\sim 25^\circ$ for 8 keV O₂⁺ bombardment to $\sim 34^\circ$ for 14.5 keV O⁺ bombardment. The thickness of stoichiometric oxide layer, d , was found to be close to the sum of the projected range, R_p , and the straggling, δR_p , of oxygen ions in Si (i.e., $d \approx R_p + \delta R_p$).²¹ We also used PROFILE²² code simulations in conjunction with high resolution Rutherford backscattering spectroscopy (HR-RBS) analysis to determine the angular and energy dependence of the sputtering coefficient of Si under oxygen ion bombardment.²¹

The formation of a nitride layer under nitrogen ion bombardment shows similar effects, since nitrogen and oxygen have similar masses and ranges in Si, show similar sputtering effects and both are chemically reactive with Si.¹³ However,

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several differences between the ion beam synthesis of silicon oxides and nitrides have been reported and related to the different structural and electrical properties of oxides and nitrides.^{13,23} The atomic density is much higher in Si_3N_4 than in SiO_2 (1.04×10^{23} atoms/cm³ and 0.68×10^{23} atoms/cm³, respectively), making the nitride a very good diffusion barrier, even for nitrogen. The low diffusivity of nitrogen in the nitride layer may result in the formation of overstoichiometric nitride layers.¹³ Moreover, high fluence ($\geq 1.4 \times 10^{18}$ cm⁻²) and high-energy (≥ 150 keV) N^+ implantation of Si at 500 °C has shown that gas-phase N_2 bubbles are formed within a N-rich Si nitride layer.^{10,24} Another consequence of the high density of Si_3N_4 is the dramatic reduction in the range of nitrogen ions in nitride, which is $\sim 65\%$ of the range of nitrogen in Si for 13.5 keV N_2^+ ions. Although both oxides and nitrides of Si charge positively under ion bombardment, the charging effects are more pronounced for Si nitrides.²⁵ The differences between the properties of Si nitrides and oxides result in different transient stages for the ion beam synthesis of Si nitride and SiO_2 layers. We have recently reported on the strong oscillations in the secondary ion yields during the transient stages of nitrogen ion bombardment of Si below the critical angle of incidence for nitride formation.^{13,26}

The formation of buried nitride layers has been studied for the high-energy nitrogen ion implantation (≥ 50 keV/ N^+ ion) of Si.^{2,10,24,27–29} Only few articles are published for bombardment using low-energy nitrogen ions (0.1–10 keV/ N^+ ion).^{2,23,30,31} The ion beam nitridation of Si with N_2^+ ions in the 100–1000 eV energy range has been investigated for the near-normal bombardment using predominantly x-ray photoelectron spectroscopy (XPS).² In another study, the ion-induced electron emission has been used as a means to investigate the energy- (2–10 keV N_2^+) and angular-dependent (0° – 84°) compositional changes of Si under nitrogen ion bombardment,³⁰ while the N content in Si-nitride layers was reported in a normalized form. The formation of overstoichiometric Si-nitride layers has been demonstrated for 12 keV N_2^+ bombardment of Si at normal incidence.²³ XPS measurements showed that this overstoichiometric nitride layer consists of Si bonded to N in the stoichiometric ratio for Si_3N_4 plus some additional nitrogen in the form of N–N bonds. The results from Ref. 23 are consistent with those from the high-energy nitrogen ion bombardment of Si at temperatures ~ 500 °C, which have demonstrated the formation of N_2 bubbles within a Si_3N_4 buried layer.^{24,28} More recently, the angular dependencies of surface composition, sputtering and ripple formation on Si under N_2^+ bombardment has been investigated for the 1.5–9 keV energy range.³¹ The results from these investigations will be revisited during the discussion of the results obtained in the present study. It is pointed out here that none of the studies using low-energy nitrogen ion bombardment have discussed the transient stages of Si-nitride formation. In fact, none of those studies have observed the effects discussed in this article.

In the present study, we report on the angular dependence of Si-nitride formation for 10 and 13.5 keV N_2^+ bombard-

ment of Si. The dynamics of the initial stages of Si-nitride formation is discussed in detail. We demonstrate the close relation between the critical angle for Si-nitride formation and the oscillations in the secondary ion yield of $^{14}\text{N}^+$, and show the influence of surface charging on these oscillations. We also provide the evidence that the surface charging is directly related to the thickness of the nitride layer, which changes periodically during the transient stages of nitridation. Finally, we show that oscillations in the secondary ion yield during the initial stages of the ion beam induced nitridation process can be adequately described by a second order differential equation.

II. EXPERIMENT

In this study we used (100) *n*-type Si wafers with resistivity of 5–10 Ω cm. Ion beam nitridation was performed in a Riber MIQ 256 secondary ion mass spectrometry (SIMS) apparatus using 10 or 13.5 keV N_2^+ ions at impact angles from 0° – 60° measured with respect to the surface normal. Additional near-normal bombardment with 5 keV N_2^+ ions was undertaken to study the energy dependence of $^{14}\text{N}^+$ oscillations. In our SIMS instrument the energy of the primary beam and its angle of incidence can be changed independently, which is an essential requirement for the type of studies we report in this article. Nitrogen ion bombardment was also performed on an Au-coated (25 nm) Si sample in order to investigate the influence of surface charging on the oscillations in secondary ion yield during the transient stages of Si-nitride formation. The primary beam (typically 0.3–2 μA) was raster scanned over an area of ~ 9 mm². Beam-induced heating effects were expected to be negligible for the low power densities (< 0.3 W cm⁻²) used in our experiments.

The nitrogen content of the surface Si-nitride layers was determined by high resolution (HR-) Rutherford backscattering spectroscopy and ion channeling (RBS-C) using 1.8 MeV He^+ ions in the glancing angle geometry.³² A beam spot of 1 mm diameter was positioned in the center of a SIMS crater using a two-axis goniometer. For channeling spectra the incident beam was aligned along the $\langle 100 \rangle$ crystallographic direction (roughly normal to the sample surface), whereas it was $\sim 7^\circ$ off axis for random spectra. The depth resolution of the detector was adjusted by varying the exit angle, ϕ . For $\phi \approx 86^\circ$, an average depth resolution of ~ 2.4 nm is obtained within the top 20 nm of the sample surface for a surface barrier detector with an energy resolution of 14 keV.³²

III. RESULTS

In SIMS, the sputter removal of surface atoms by the primary ion beam at the one time provides the analytical signal and gives the information about the in-depth distribution of impurities. This unique feature of the SIMS technique enabled us to monitor the response of the system simultaneously with the buildup of nitrogen in Si, the formation of a buried nitride layer and its extension to the surface.

Figure 1 illustrates the change in N content, y , in Si-nitride layers (SiN_y) as a function of incident angle for 10

FIG. 1. Angular dependence of nitrogen content in thin nitride layers formed at the Si surface after bombardment with 10 or 13.5 keV N_2^+ ions. The data points were extracted from high resolution RBS measurements. The broken line indicates the N content in stoichiometric Si_3N_4 . Ion fluences of $\sim 8.5 \times 10^{16}$ and $\sim 2 \times 10^{17}$ N/cm² were used for $\theta = 60^\circ$ and $\theta = 0^\circ$, respectively, and were quite similar for both energies.

(open circles) and 13.5 keV N_2^+ (solid circles) bombardments. Our estimates reveal that fluences of $\sim 8.5 \times 10^{16}$ and $\sim 2 \times 10^{17}$ N/cm² were used for $\theta = 60^\circ$ and $\theta = 0^\circ$, respectively. These values were very similar for both energies. It is pointed out here that the determination of an exact value of ion fluence is limited by the accurate determination of the area of craters. The SIMS craters are trapezoidal in shape and their dimensions change when the angle of incidence is varied. The broken line in Fig. 1 indicates the level of N in the stoichiometric Si_3N_4 film (i.e., $y = 1.3$). Both plots show three distinct stages in the nitridation process determined by the two critical angles for the Si-nitride formation. For 10 keV N_2^+ bombardment, substoichiometric layers are formed above the critical angle $\theta_{c1} \approx 40^\circ$ corresponding to Si_3N_4 formation. The N content increases above its stoichiometric level for angles of incidence below θ_{c1} and reaches a saturation level ($y \sim 1.9$) below the critical angle $\theta_{c2} \approx 28^\circ$. The angular dependence of y is similar for 13.5 keV N_2^+ bombardment except that the critical angles are shifted to the higher impact angles ($\theta_{c1} \approx 45^\circ$ and $\theta_{c2} \approx 30^\circ$), and a higher saturation level of nitrogen of ~ 2.3 is reached.

The data points in Fig. 1 were obtained by simulating the random and channelled HR-RBS spectra using RUMP,³³ in a way previously reported in Refs. 19 and 21 for oxide formation. Typical channeling and random HR-RBS spectra taken from SIMS craters using an exit angle $\phi \approx 84^\circ$ are shown in Fig. 2 for 10 keV N_2^+ bombardment. Figure 2(a) shows spectra obtained from a crater created at the normal incidence, which demonstrate that a nitride layer extending to the surface is formed for these bombardment conditions. The solid lines overlaying the experimental data points correspond to the RUMP simulations of the structure shown in the inset of Fig. 2(a), and show the formation of a 7.5-nm-thick overstoichiometric $Si_3N_{5.7}$ (equivalently $SiN_{1.9}$) layer for 10 keV N_2^+ bombardment of Si at 0° incidence. The surface peak be-

FIG. 2. Typical random and channelled HR-RBS spectra taken from the bottom of SIMS craters formed by 10 keV N_2^+ bombardments at (a) 0° and (b) 60° incidence. The solid lines overlaying the experimental data points correspond to the RUMP simulations of the structures shown in the insets.

tween channels 292 and 297 is due to the presence of oxygen in our sample in the form of a N-rich oxynitride layer ($Si_3N_{4.2}O_x$) underlying a very thin oxide layer ($SiO_{0.71}$) at the surface. RUMP simulations show that the oxygen content in the oxynitride layer decreased from $x = 0.4$ at the oxide/oxynitride interface to $x = 0$ at the oxynitride/ $Si_3N_{5.7}$ interface. It is pointed out here that no special precautions were taken to prevent oxidation of our samples between SIMS bombardments and HR-RBS analysis. Samples were stored in air for up to one week between measurements. The overstoichiometric nitride layer is believed to extend all the way to the surface after SIMS bombardments in the low 10^{-10} Torr pressure range. The channeling spectrum in Fig. 2(a) shows the presence of a heavily damaged Si layer below the $Si_3N_{5.7}$ layer. A comparison between the channelled and random spectra indicates that the damaged layer is most probably amorphous, and, judging from the tail of the nitrogen profile at the back edge of the nitride, that it contains a significant amount of nitrogen. Figure 2(b) illustrates the channeling and random spectra from a SIMS crater created with 10 keV N_2^+ ions at 60° incidence. The RUMP simulations

FIG. 3. Nitrogen signal measured during bombardment of Si with (a) 10 keV N_2^+ and (b) 13.5 keV N_2^+ ions at different angles of incidence.

(solid lines) reveal that the surface nitride layer is substoichiometric (SiN_y , $y < 1.3$), and can be adequately modeled using a linearly changing nitrogen content from $y = 0.43$ at the surface to $y = 0$ at the SiN_y/c -Si interface. RUMP simulations of HR-RBS data were performed in a similar way to determine the angular dependence of y for Si-nitride layers formed by 13.5 keV N_2^+ bombardments.

We now turn to the dynamics of the ion beam nitridation process. Recently, we have shown that the bombardment of Si with nitrogen ions at the normal incidence eventually transforms the surface into a continuous nitride layer, inducing a series of transient oscillations in the yield of secondary ions.^{13,26} In Fig. 3 we show the angular dependence of the oscillations in the $^{14}N^+$ yield for (a) 10 keV N_2^+ and (b) 13.5 keV N_2^+ bombardment of Si. As the incidence angle is increased from 0° to 60° , the oscillations in both cases become less intensive and eventually disappear above the critical angle 28° and 30° for 10 keV N_2^+ and 13.5 keV N_2^+ bombardments, respectively. This behavior correlates nicely with the angular dependence of Si-nitride formation shown in Fig. 1. In particular, the oscillations start to appear at the critical angle θ_{c2} and correspond to the formation of overstoichiometric nitride layers with fixed N content.

The positions '1' and '2' marked by the arrows on the SIMS profile for 0° incidence in Fig. 3(a) correspond to the

FIG. 4. SIMS in-depth profiles of Si-nitride layers produced at the normal incidence by 5 and 14.5 keV N_2^+ bombardment to two different fluences corresponding to the similar positions as 1 and 2 in Fig. 3(a).

peak position of the first oscillation and the dynamic equilibrium condition (no more oscillations), respectively. Here, dynamic equilibrium is defined by the balance between the sputter removal of the nitride layer at the surface and its growth at the internal interface by implantation of nitrogen ions. These positions, therefore, correspond to two different bombardment fluences. We have determined the depth profiles of thin nitride layers produced at the normal incidence with either 5 or 14.5 keV N_2^+ bombardment to the two fluences described by positions 1 and 2. For 14.5 keV N_2^+ bombardment, we estimate fluences of $\sim 2.6 \times 10^{17}$ and $\sim 8 \times 10^{17}$ N/cm² for positions "1" and "2," respectively. The estimated fluences for 5 keV N_2^+ bombardment are $\sim 1.5 \times 10^{17}$ N/cm² (position 1) and $\sim 4.5 \times 10^{17}$ N/cm² (position 2). The four SIMS craters were produced on the same Si substrate, and the bottom of these craters was profiled internally using 6 keV Cs^+ ions at 55° incidence. Figure 4 illustrates the nitrogen profile (represented by yield of SiN^- ions) from these nitride layers. The solid curves [corresponding to the equilibrium position 2 in Fig. 3(a)] provide the final thickness of the nitride layers that extend to the surface. By defining the SiN_y/Si interface at the point where the $^{42}SiN^-$ yield drops by $1/e$ of its peak value, the thicknesses of Si-nitride layers are found to be ~ 13.8 and ~ 32.3 nm for 5 and 14.5 keV N_2^+ , respectively. Figure 4 also shows that the final nitride layer is both slightly thinner and contains less N than the layer at position 1 (broken line in Fig. 4). This may indicate the lower amount of nitrogen within the final layer. Furthermore, a comparison between the two sets of curves in Fig. 4 indicates that the N content of nitride layers is higher for the 14.5 keV N_2^+ than for the 5 keV N_2^+ bombardment. This result is in good qualitative agreement with that depicted in Fig. 1, which shows a higher saturation level of N for the higher beam energy.

It is well known that the surface of insulating layers, such as oxides and nitrides, charges up positively under ion bombardment, with the effect being more severe for Si nitride.²⁵

FIG. 5. Nitrogen signal measured from a bare and an Au-coated Si sample during bombardment with 10 keV N_2^+ at 0° incidence. The oscillations are suppressed as the Au coating provides a conductive path for the surface charge.

We have, therefore, investigated the influence of surface charging on the oscillations in secondary ion yields during the transient stages of nitridation. Figure 5 illustrates the yield of $^{14}N^+$ ions from bare and Au-coated Si during bombardment with 10 keV N_2^+ at the normal incidence. The Au coating provides a conductive path for charge removal from the Si-nitride layer and suppresses the oscillatory response of secondary ion yield. The results in Fig. 5 reveal that the oscillations in secondary ion yield shown in Fig. 3 are closely related to the surface charging and discharging of the nitride layer formed below the critical angle θ_{c2} .

The oscillatory response in secondary ion yields during the transient stage of ion beam nitridation can be modeled using the second order differential equation describing the impulse response of a damped system.³⁴ This equation together with its solutions for the cases when the system is underdamped and overdamped are given in Appendix A.³⁴ The differential equation is described in terms of the charge stored by the insulating nitride layer under ion bombardment. Changes in the surface charge, or the potential drop across the surface nitride layer, as described by the equations in Appendix A, will produce corresponding variations in the yield of secondary ions sputtered from the surface. Hence, the secondary ion signal provides the response of the nitride layer under ion bombardment. We have used Eqs. (A2) and (A3) [see Appendix A] to simulate selected signals from Fig. 3. The SIMS signals were first normalized to their respective dynamic equilibrium yields. Figure 6(a) shows the experimental results for bombardment at 35° (open circles), together with the fitting (solid curve) to Eq. (A2), while Figs. 6(b) and 6(c) show the fitting of signals obtained at 28° and 20° , respectively, to Eq. (A3). In Fig. 7 we illustrate the dynamic response of the Si-nitride layer under bombardment at the normal incidence with 5, 10, or 13.5 keV N_2^+ ions. Again, the experimental data are shown in open circles, while all the fits to Eq. (A3) are shown in solid curves. The

FIG. 6. Buildup profiles of nitrogen (open circles) obtained at (a) 35° , (b) 28° , and (c) 20° incidence during 10 keV N_2^+ bombardment of Si. Solid lines are fits of experimental data to (a) Eq. (A2) and (b), (c) Eq. (A3). The nitrogen signals are normalized to their respective steady-state yields. The time scale has been adjusted to correspond to the moment when the buried nitride layers intersect the surface. Insets show values of the fitting parameters.

values of the fitting parameters ζ and ω_0 are shown in the insets of Figs. 6 and 7. It should be noted here that the time scales in Figs. 6 and 7 have been adjusted to correspond to the moment when the buried nitride layers intersect the surface. In other words, surface charging starts to have an effect on the secondary ion yield only when the nitride layer extends to the surface.

IV. DISCUSSION

The ion beam nitridation process is fairly similar to the ion beam oxidation of Si. Bombardment with low-energy N_2^+ ions results in the buildup of nitrogen below the surface and the simultaneous sputter removal of the Si surface. The maximum concentration of nitrogen, therefore, depends on the relative rates of nitrogen buildup and sputtering, which, in turn, depend on the primary beam energy and angle of incidence. The sputtering yield decreases with the decreasing angle of incidence for a given primary beam energy. The N content in nitride layer, therefore, increases with the decreasing angle of incidence as shown in Fig. 1. At the critical angle θ_{c1} a stoichiometric nitride layer is formed. A recent study of ion beam nitridation of Si has proposed that the substoichiometric Si-nitride layer most probably consists of α - Si_3N_4 clusters embedded in the Si matrix.³¹ This proposition is not based on experimental evidence but rather follows

FIG. 7. Dynamic response of Si-nitride layer under bombardment at the normal incidence with (a) 5, (b) 10, or (c) 13.5 keV N_2^+ ions. Experimental data are shown by open circles and the solid curves represent fits to Eq. (A3). Insets show values of fitting parameters.

the argument that N has both a low solubility and diffusivity in Si, together with the stronger binding of Si–N in comparison with Si–Si. Once the buried layer has formed, the difference between oxygen and nitrogen bombardment becomes significant because of the large difference in atomic density between SiO_2 and Si_3N_4 . The dense nitride layer acts as a diffusion barrier for impurities, including nitrogen. Below θ_{c1} excess nitrogen ions are trapped within the buried Si-nitride layer to produce overstoichiometric films. It is worth noting that the presence of N–N bonds in overstoichiometric Si-nitride layers formed at the normal incidence with 12 keV N_2^+ ions has previously been demonstrated.²³ The decrease in sputtering rate below θ_{c1} results in the formation of progressively more N-rich overstoichiometric layers until the critical angle θ_{c2} is reached. According to the results reported in Ref. 30 there is no significant difference between the sputtering yield below the critical angle θ_{c2} . Furthermore, the penetration depth of nitrogen ions does not change significantly with the decreasing angle of incidence below θ_{c2} . The similar sputtering yield and penetration depth of nitrogen ions below θ_{c2} consequently results in the saturation of nitrogen content in overstoichiometric nitride layers as depicted in Fig. 1. The angular dependence of the nitridation of Si using 10 keV N_2^+ bombardment is consistent with previous findings.¹³ Furthermore, the sputtering yield of Si by 9

keV N_2^+ ions is almost constant for $\theta < \sim 30^\circ$, and shows a pronounced increase above $\sim 40^\circ$.³¹ Such angular dependence in sputtering yield corresponds remarkably well with the three stages of nitridation described above.

The shifts in θ_{c1} from $\sim 40^\circ$ to $\sim 45^\circ$, and in θ_{c2} from $\sim 28^\circ$ to $\sim 30^\circ$ for 10 and 13.5 keV N_2^+ , respectively, are explained by the energy dependence of the range of nitrogen ions. The projected range, R_p , and straggling, δR_p , of nitrogen ions increase with the increasing primary beam energy. For instance, R_p and δR_p for the normal incidence in Si change from 15.4 and 6.9 nm to 20.2 and 8.9 nm when the energy of the nitrogen beam changes from 10 to 13.5 keV N_2^+ , respectively.³⁵ This implies that the buildup of nitrogen takes place deeper below the surface for 13.5 keV N_2^+ bombardment. In addition, the sputtering coefficients in the 0 – 40° range do not change significantly as reported in Ref. 31. Consequently, nitride layers with the same nitrogen content can be formed at the higher bombardment energy while increasing the sputtering rate, that is, by increasing the angle of incidence. The increased penetration depth also leads to a higher saturation level in layers below θ_{c2} for 13.5 keV N_2^+ bombardment (Figs. 1 and 4).

It is worth noting here that the formation of overstoichiometric compound during nitridation is in contrast to the ion beam oxidation of Si. The ion beam oxidation of Si does not produce overstoichiometric oxide layers since any excess O, being mobile in SiO_2 , readily diffuses to the Si/ SiO_2 interfaces or into vacuum. There are, however, a few similarities between the ion beam nitridation and oxidation of Si. First, the critical angles θ_{c2} , below which there is a saturation of N content in overstoichiometric nitride layers (Fig. 1), correspond remarkably well with those for the formation of SiO_2 layers.²¹ Second, the value $(R_p + \delta R_p)$ obtained from transport of ions in matter (TRIM) simulations³⁵ in Si is 13.7 and 31.4 nm for 5 and 14.5 keV N_2^+ ions, respectively. These values agree very well with those extracted from the SIMS profiles in Fig. 4 (~ 13.8 and ~ 32.2 nm after 5 and 14.5 keV N_2^+ bombardments, respectively). We have previously shown that the thickness of SiO_2 layers was also $\sim (R_p + \delta R_p)$ for oxygen ions implanted into Si.²¹ The thickness of nitride layer in Fig. 2(a) is less than the value $(R_p + \delta R_p) = 23.4$ nm for 10 keV N_2^+ bombardment at 0° incidence, which appears to contradict the SIMS results shown in Fig. 4. The RBS-C spectra shown in Fig. 2(a) were obtained from a SIMS crater bombarded to a fluence at least two times the threshold required for overstoichiometric nitride layer formation. The Si-nitride layer thickness is, therefore, determined by the penetration of nitrogen ions into the $Si_3N_{5.7}$ layer, and not Si, which results in a thinner nitride layer. The similarities between the ion beam oxidation and nitridation of Si are related to their similar penetration depths and sputtering yields in Si.

The dynamics of the transient stage of the nitridation process is now discussed in qualitative terms. The transient stage of ion beam nitridation of Si exhibits oscillations in the secondary ion yields below the critical angle θ_{c2} as shown in Fig. 3. Furthermore, as illustrated in Fig. 5, the oscillations are closely associated with surface charging of the nitride

layer during ion bombardment. The results in Figs. 6 and 7 show that the dynamics of the transient stages of nitridation process is analogous to the impulse response of a damped oscillatory system.

The surface of the nitride layer charges positively because of the large emission coefficient of electrons from the insulating surfaces under ion bombardment. The positive charge at the surface induces accumulation of an equal number of electrons at the nitride/Si interface. This polarization results in the dielectric behavior of the nitride layer, which effectively acts as a capacitor. An energy filter in our ion microprobe allows only the collection of secondary ions with a predetermined kinetic energy within a small bandwidth (~ 5 eV). Based on our previous measurements of the energy distribution of secondary ions collected from the bombarded Si-nitride layer,¹⁵ we estimate that a potential drop across the nitride layer of up to a few tens of volts would be sufficient to produce the oscillations shown in Figs. 3, 5, 6, and 7. Hence, we can safely conclude that the surface charging of the Si-nitride layer under bombardment does not significantly affect the energy of the primary ion beam (order of few keV). The charging and discharging of the Si-nitride layer can be explained by the large difference between the penetration depth of the primary ions in Si and the much denser Si-nitride layer.

The transformation of the Si surface into a nitride layer under N_2^+ bombardment produces a dramatic change in the density of the near-surface layer as mentioned earlier. Nitrogen ions are initially implanted into the Si matrix to form a buried overstoichiometric nitride layer with a thickness corresponding to position 1 in Fig. 3(a) (i.e., thickest nitride layer as per results in Fig. 4 and Ref. 13, and also highest N content as shown in Fig. 4). Following the simultaneous sputtering of the surface, this buried layer recedes to the surface. The intensity of secondary ions increases up to this point (first peak in oscillations). When the nitride layer intersects the surface, the range of N ions is reduced below the thickness of the nitride layer. For the primary beam energies used in this study, the range of N ions in Si_3N_4 is only $\sim 65\%$ of their range in Si. It is pointed out here that the reduction in penetration depth of N ions may also be influenced by the N content in overstoichiometric nitride layers. Unfortunately, the range and straggling of nitrogen ions in overstoichiometric nitride layers with varying N content cannot be determined using TRIM simulations since their densities are not known. This results in both the accumulation of excess N within the nitride layer and the surface charging since there is no conductive path through the nitride layer. This surface charging results in a shift in the energy distribution of sputtered secondary ions, and a corresponding decrease in the number of ions that are collected.¹⁵ The generation of charge buildup, caused by bombardment of insulating samples with energetic particles, and its role in altering the relative secondary ion currents and reducing their absolute values, is a well-known phenomenon in SIMS.³⁶ The first trough in the secondary ion signal shown in Fig. 3(a) for the normal incidence corresponds to the situation of maximum surface

charging. However, simultaneous sputtering of the surface reduces the thickness of the N-rich nitride layer. When the thickness of the nitride layer becomes comparable to the range plus straggling ($R_p + \delta R_p$) of N ions in Si nitride, the ions penetrate into the underlying Si and a conductive path for charge is restored. This corresponds to an increase in the intensity of secondary ions and also a gradual increase in the thickness of the Si-nitride film. Once the thickness of the layer is just above the range of N ions in the Si-nitride layer (second peak in oscillations) surface charging causes a decrease in secondary ion intensity. At this point N ions are implanted into an overstoichiometric nitride and sputtering takes over to reduce the thickness of the film. This scenario repeats itself until a steady-state situation is reached (i.e., position 2).

Indeed, the results shown in Fig. 4 demonstrate the difference between the thickness of the layer at the peak position of the first oscillation (position 1) and the final layer thickness (steady-state position 2). Similar results have previously been obtained using high resolution RBS-C measurements.¹³ It has been shown that the thickness of nitride layer is thickest around the peak of the first oscillation (penetration of N ions in Si) and is continuously reduced thereafter to reach its steady-state value (penetration of N ions in Si nitride).¹³ Furthermore, as also shown in Fig. 4, a reduction in thickness of the nitride layer is accompanied by a reduction in its N content of the overstoichiometric nitride layer. The variation in film thickness eventually dies out and a steady state situation prevails when the layer thickness is maintained at $\sim (R_p + \delta R_p)$. Hence, the combination of reduced range of N ions in Si-nitride and sputtering tries to maintain the thickness of nitride layer constant. Effectively the surface charging of the nitride layer under ion bombardment is modulated resulting in a series of oscillations in secondary ion yield until dynamic equilibrium is reached. In other words, the thickness and, hence surface charging of the Si-nitride layer is reduced from a maximum corresponding to position 1 in Fig. 3 to its steady-state value at position 2 through a series of cycles, in order to maintain a constant secondary ion current.

The results shown in Figs. 1 and 3 demonstrate that the surface charging effect, and, hence, oscillations in secondary ion signal, becomes more significant below θ_{c2} , most probably because of the much reduced penetration depth of nitrogen ions in these films. In addition, the oscillation is less pronounced at the higher bombardment angles, since the higher sputtering rate limits large fluctuations of film thickness, such that surface charging effects are reduced. The surface nitride layer under ion bombardment can be adequately described by a second order differential equation that characterizes a damped oscillatory system.

At the critical angle θ_{c2} , the surface charging effects become significant, thus increasing the quality factor, Q ,³⁴ (Appendix A) or alternatively, giving $\zeta < 1$. Oscillations can be described by Eq. (A3) as illustrated in Figs. 6 and 7. The change of intensity and damping of oscillations shown in Figs. 6(b) and 6(c) may be explained in the following way. For these low angles, the thickness of nitride layer does not

change significantly, while the stoichiometry remains almost the same (see Fig. 1). The angular dependence of oscillations in secondary ion yield, therefore, corresponds to the angular dependence of the sputtering coefficient for 10 keV N_2^+ bombardment of Si, and is in good agreement with the results reported in Ref. 31. The transient response of the N_2^+ -bombarded Si-nitride system in Figs. 6(b) and 6(c) could be adequately fitted by varying ζ while keeping ω_0 at almost constant value ($\omega_0 \sim 0.102\text{--}0.104\text{ s}^{-1}$). The period of oscillation is described by Eq. (A4) (Appendix A) which becomes $\sim 2\pi/\omega_0$ for bombardment below 28° , i.e., $\zeta < 0.4$. The almost constant value of ω_0 corresponds to the similar ranges, and, hence, thickness of nitride layers for 10 keV N_2^+ in Si for 28° and 20° incidence (~ 13.5 and ~ 14.8 nm, respectively, from TRIM simulations). The disappearance of oscillations for bombardment with nitrogen ions above the critical angle θ_{c2} is attributed to the fact that the relatively high sputtering rate prevents oscillations in secondary ion yield [Fig. 6(a)], and the system has a low quality factor (i.e., $\zeta > 1$). In other words, the lowering in sputtering rate below the critical angle θ_{c2} effectively extends the equilibration time, and gives a higher quality factor (i.e., $\zeta < 1$) to the system. The experimental data in Fig. 7 can also be adequately fitted using Eq. (A3) (Appendix A), but discussion of results is limited by following unknown parameters.

The detailed analysis of fitting parameters in Figs. 6 and 7 is complicated by several unknowns, such as the influence of N content of Si-nitride layers on the range of nitrogen ions and surface charging effects (i.e., dielectric property of nitride layer). Furthermore, the sputtering rate of overstoichiometric Si-nitride layers with different N content is not known. The results in Fig. 7, however, demonstrate that surface charging effects are the smallest for the 5 keV N_2^+ bombardment. Further analysis is also complicated by the fact that the primary beam current, which influences the sputtering rate for a fixed SIMS crater size, could not be kept constant in our energy dependence study of the ion beam induced nitridation of Si.

V. CONCLUSIONS

We have studied the energy and angular dependence of the ion beam induced nitridation of Si using SIMS and HR-RBS. For 10 keV N_2^+ bombardment, a stoichiometric nitride layer is formed at the critical angle $\theta_{c1} \approx 40^\circ$. At smaller angles of incidence overstoichiometric Si-nitride films are formed, while a saturation level in the N content ($y \sim 1.9$ in SiN_y) is reached below the critical angle $\theta_{c1} \approx 28^\circ$. The critical angles are shifted to $\theta_{c1} \approx 45^\circ$ and $\theta_{c2} \approx 30^\circ$ for 13.5 keV N_2^+ bombardment predominantly due to the larger penetration depth of ions. A higher saturation level, $y \sim 2.3$, is obtained for 13.5 keV N_2^+ bombardment. The energy dependence of θ_{c2} is similar to that of the critical angle for the formation of an SiO_2 layer. The thickness of nitride layer is approximately equal to the sum of projected range and straggling of N ions in Si. We have shown that oscillations in the nitrogen ion signals are obtained for bombardment below θ_{c2} . These oscillations are directly related to the charging of

the surface nitride under ion bombardment. Finally, we have demonstrated the nitride layer under ion bombardment can be treated as a damped oscillatory system.

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APPENDIX

The damped oscillatory system can be described by the second order differential equation³⁴

$$\ddot{q} + 2\zeta\omega_0\dot{q} + \omega_0^2q = Q_0, \quad (A1)$$

where ζ is the damping factor, ω_0 the natural frequency of the system, and q is the charge on the Si-nitride insulating layer. The damped system is excited by the impulse Q_0 , which in our case is analogous to the constant primary ion beam current. For $\zeta > 1$, the system is overdamped and the solution of (1) is³⁴

$$\begin{aligned} \frac{q}{Q_0} = 1 - \exp^{-\zeta\omega_0 t} & \left[\cosh(\omega_0 t \sqrt{\zeta^2 - 1}) \right. \\ & \left. + \frac{\zeta}{\sqrt{\zeta^2 - 1}} \sinh(\omega_0 t \sqrt{\zeta^2 - 1}) \right], \end{aligned} \quad (A2)$$

and for $\zeta < 1$, the system is underdamped with the solution³⁴

$$\begin{aligned} \frac{q}{Q_0} = 1 - \exp^{-\zeta\omega_0 t} & \left[\cos(\omega_0 t \sqrt{1 - \zeta^2}) \right. \\ & \left. + \frac{\zeta}{\sqrt{1 - \zeta^2}} \sin(\omega_0 t \sqrt{1 - \zeta^2}) \right]. \end{aligned} \quad (A3)$$

For the underdamped solutions, the period of oscillations, T , is given by

$$T = 2\pi/\omega_0\sqrt{1 - \zeta^2}. \quad (A4)$$

The quality factor of the system is defined as 2π times the mean stored energy, divided by the work done per cycle. If we consider a circuit with a high Q , that means that the amount of energy stored in the oscillation is very large compared with the amount of work done per cycle by the machinery that drives the oscillations. For weak damping, we have³⁴

$$Q \approx 1/\zeta. \quad (A5)$$

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