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Modification of Optical Properties of Silicon Nitride Films on Si(100) by Ion Beams

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We have measured the refractive index change of Si_3N_4 films (0.28 μm) on Si (100) substrate induced by irradiation with 0.1 and 0.5 MeV N^+, and 0.1 MeV Ne^+ and Ar^+ ions. We have observed that the refractive index of both unirradiated and irradiated films monotonically decreases with increasing the photon wavelength from 0.4 to 1.7 μm. We find that the refractive index at 0.5 μm increases by 2.5% and 6% for 0.1 MeV N at 0.9 $x10^{17}/cm^2$ and 0.5 MeV N at $2.0x10^{17}/cm^2$, respectively. The modifications of the refractive index are discussed in terms of the electronic structure modifications due to rearrangement of bonds and atoms, implants-inclusion in the films and composition change by ion irradiation.
Key words; Ion irradiation, Refractive index, Si_3N_4 films, Electronic structure modification

1. INTRODUCTION

Silicon nitride (Si_3N_4) films have applications such as optical devices on Si [1-2], waveguides on Si [3-4], anti-reflection coatings on amorphous (a-) SiO_2 [5,6] and graded-index filters on a-SiO_2 [7]. In these applications, the refractive index is an important factor. Thus, modification of the refractive index by ion beams is of interest. Recently, it has been reported [8,9] that the refractive index of the Si_3N_4 films on a-SiO_2 substrate decreases after ion irradiation. It is worthwhile to collect more data for applications and understanding of ion-induced modifications.

In this work, we have investigated ion irradiation effects on refractive index of Si_3N_4 films on Si(100) substrates. The results will be compared with those reported [8,9]. The modifications of the refractive index are discussed in terms of the electronic structure modifications and density modification.

2. EXPERIMENT

Samples are chemically-grown Si_3N_4 films on Si (100) substrates (CREE MATERIALS product). The films were irradiated with 0.1 MeV N^+, Ne^+ and Ar^+, and 0.5 MeV N^+ ions at room temperature in vacuum of $\sim 10^{-7}$ Torr. The refractive index was measured using ellipsometry before and after ion irradiation. The Si_3N_4 film composition and thickness were analyzed by 1.8 MeV He Rutherford backscattering spectroscopy (RBS) with the normal incidence and scattering angle of 160°. Nuclear reaction analysis (NRA), $^{16}O(d, \alpha)^{14}N$ and $^{12}C(d, p)^{13}C$, with 1.2 MeV d was employed to detect oxygen and carbon impurities, using NRA cross sections of 5.3 and 120 mb/sr, respectively. ZBL stopping powers [10] with film density of $4.11x10^{22}$ Si/cm^3 (3.2 g/cm^3) were used for RBS and NRA. The film thickness on Si(100) is 0.28 μm. X-ray diffraction shows that the Si_3N_4 films are amorphous before and after ion irradiation.

3. RESULTS

3.1 Refractive index

The refractive index (n) vs the photon wavelength (λ) from 0.4 to 1.7 μm is shown in Fig. 1. The mean refractive index of four unirradiated Si_3N_4 films on Si(100) is fitted to the Cauchy model: $n=1.9676 + 0.01684/\lambda^2$ (λ in μm) and n varies from 2.07 to 1.97.

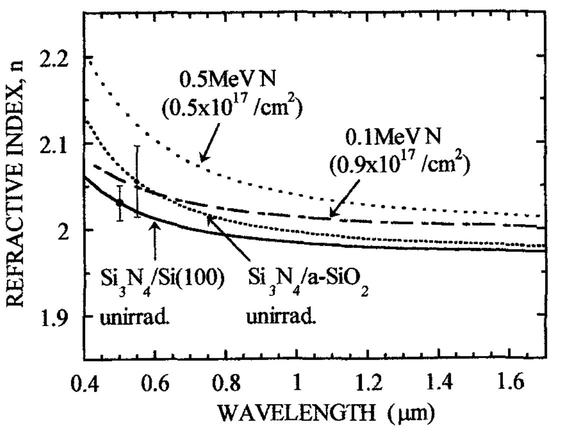

Fig. 1 Wavelength dependence of the refractive index of unirradiated Si_3N_4 *films on Si(100) substrates* (—), and that of films irradiated with 0.1 MeV N at $0.92x10^{17}/cm^2$ (-·-) and 0.5 MeV N at $0.5x10^{17}/cm^2$ (····). Also shown is the refractive index of unirradiated Si_3N_4 films on a-SiO_2 substrate (---) [8,9].

The sample-to-sample variation of the refractive index of unirradiated films appears to be within 1%. The mean refractive index at λ=0.83 μm is 1.99 and agrees with the reported values of 2.07, 2.0 and 2.01 for silicon nitride films on Si [11], Si(111) [12] and SiO_2 [13] substrates, respectively. For comparison, the refractive index is shown for unirradiated Si_3N_4 films

(~0.2 μm) on a-SiO_2 substrate, which were prepared by using RF-sputter deposition method with pure N_2 gas [8,14]. The sample variation in this case was ~ 2% and the refractive index of these films is slightly larger than Si_3N_4 films on Si(100). It is found that the refractive index of Si_3N_4 films on Si(100) increases after ion irradiation and has a similar wavelength- dependence to that before irradiation.

The representative refractive index at λ=0.5 μm of the irradiated films is normalized with respect to that of the unirradiated films and the results are shown in Fig. 2. For the films on Si(100), the refractive index increases after irradiation of 0.1 MeV N, Ne and Ar, and 0.5 MeV N ions, while the refractive index of the films on a-SiO_2 decreases by 0.1 MeV N ion irradiation [8,9]. The ion-induced change of the refractive index, Δn=n(irrad)/n(unirrad)-1 in % is summarized in Table I for relatively high fluence of each ion.

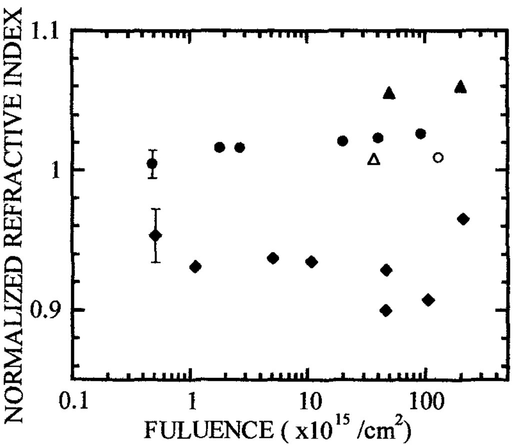

Fig. 2 Normalized refractive index of Si_3N_4 films on Si(100) substrates (refractive index at λ=0.5 μm of irradiated film divided by that of unirradiated films) vs fluence for 0.1 MeV N (●), 0.5 MeV N (▲), 0.1 MeV Ne (Δ) and 0.1 MeV Ar (o) ion irradiation. Also shown is the fluence dependence of normalized refractive index of Si_3N_4 films (~ 0.2 μm) on a-SiO_2 substrates irradiated with 0.1 MeV N ion (♦) [9].

3.2 Composition

The composition (N/Si) of unirradiated Si_3N_4 films is 4.0/3.0 ± 5%. After 0.1 MeV N ion irradiation at $1.2x10^{17}/cm^2$, decrease of the Si composition by 23% at most is seen in Fig. 3a. Inclusion of irradiated Ne without significant composition-change is observed for 0.1 MeV Ne ion irradiation at $0.36x10^{17}/cm^2$.

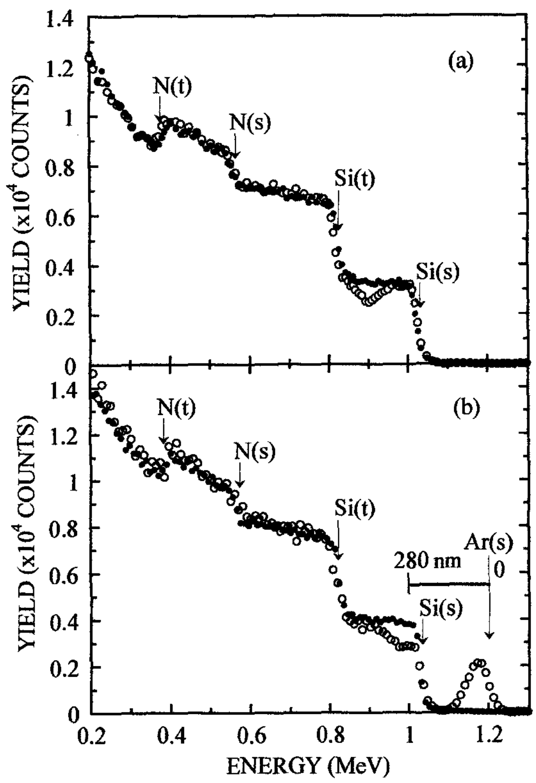

Fig. 3 (a) 1.8 MeV He RBS spectra for Si_3N_4 films on Si(100) substrate; (●) unirradiated and (○) irradiated with 0.1 MeV N at $1.2x10^{17}/cm^2$. The film surface is denoted by the leading edges of Si(s) and N(s). The trailing edges labeled as Si(t) and N(t) denote the film-substrate interface. (b) Similar to (a) except for irradiation with 0.1 MeV Ar at $1.3x10^{17}/cm^2$.

Table I: Experimental and estimated refractive index change in Si_3N_4 films on Si(100) induced by ion irradiation.

Ion		N	Ne	Ar	N
Energy (MeV)		0.1			0.5
Fluence ($10^{17}/cm^2$)		0.92	0.36	1.3	2.0
dpa		7.5	5.6	36	4.1
Experimental Δn (%)		+ 2.5	+ 1	+ 1	+ 6
Estimated Δn (%)	(a) Rearrangement	-9	-9	-9	-9
	(b) Implants-inclusion	+7.5	+7.3	+7.5	0
	(c) Composition	-5	0	-8	-1
	Total (a+ b+ c)	-6.5	-1.7	-9.5	-10

(a) -9% for dpa>0.8, (b) +7.5(1-exp(-10xFluence))%, Fluence in $10^{17}/cm^2$, (c) -3% per 5% Si deficiency.

For 0.1 MeV Ar ion irradiation at $1.3x10^{17}/cm^2$ shown in Fig. 3b, inclusion of irradiated Ar and the decrease of the Si composition by 30% are observed. The Si composition near the surface decreases by a few % after 0.5 MeV N irradiation at $2.0x10^{17}/cm^2$. NRA shows oxygen less than the detection limit of ~0.1%, and carbon less than $10^{16}/cm^2$ near the surface. These impurities would not have serious effects.

The sputtering yields (Ys) of Si_3N_4 films on Si(100) with 0.1 MeV Ne and Ar ion irradiation were obtained to be 0.4 and 1.3, respectively [8]. With the linear relationship between Ys and the nuclear stopping power near the film surface, Ys for 0.1 and 0.5 MeV N ion irradiation are estimated to be 0.17 and 0.058, respectively. For 0.1 MeV Ar ion irradiation at $1x10^{17}/cm^2$, the decrease in the film thickness is 14 nm and this would be insignificant in this study.

4. DISCUSSION

The refractive index may be modified by the electronic structure modifications due to composition change, implants-inclusion and rearrangement of bonds and atoms, via the energy deposition (rearrangement effect) by ion irradiation [15]. The rearrangement effect includes bond modifications, defect formation etc. The decrease in the film density will lead to increase in the refractive index [15]. The density modification by ion with the energy in the 0.1 MeV regions would be scaled with the nuclear energy deposition, i.e, dpa scaling would hold. However, the present results are not the case (the change in the refractive index does not simply scale with dpa as described below).

In order to evaluate each contribution, the ion depth-profiles and energy deposition are required. Ion range distribution and depth profiles of nuclear energy deposition Snd (subtracted the ionization energy loss by recoils) calculated using TRIM1997 are shown in Fig. 4. Relevant quantities, i.e., projected range, average Snd over the film thickness (d) of 0.28 μm (for Rp>d) or the projected range (for Rp<d) and dpa are listed in Table II. The threshold displacement energy Ed is taken as 50 eV [16] for dpa calculation.

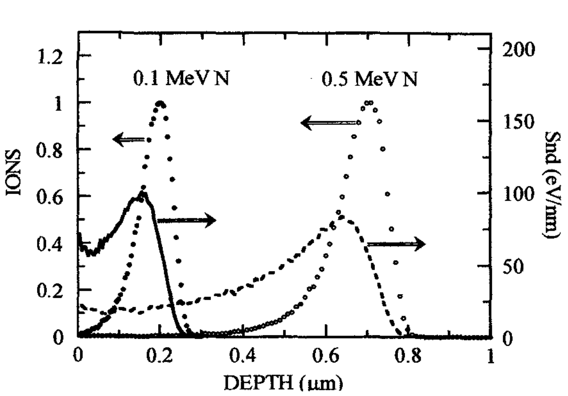

Fig. 4 Range profiles of 0.1 MeV N (•), 0.5 MeV N (○), and nuclear energy deposition Snd of 0.1 MeV N (—) and 0.5 MeV N (- - -) in Si_3N_4, calculated using TRIM [10].

Firstly, the rearrangement effect is described. It has been reported that for 0.1 MeV N irradiation up to $2x10^{17}/cm^2$ on Si_3N_4 (0.2 μm)/a-SiO_2, there is no *implants-inclusion* effect and no composition change [8]. It appears [9] that the value of Δn saturates at -9% for fluence greater than $1x10^{16}/cm^2$ (or dpa>0.8) shown in Fig. 2. The saturation value is used for the following discussion. For the fluence > $2x10^{17}/cm^2$, the refractive index starts to increase and the reason is not understood at present.

Table II: Ion species, their energies, projected ranges (Rp), average nuclear energy depositions Snd and the displacements per atom (dpa).

Ion	N	Ne	Ar	N
Energy (MeV)		0.1		0.5
Projected range (μm)	0.18	0.15	0.077	0.66
Average Snd (eV/nm)	78	150	270	20
dpa ($1x10^{17}/cm^2$)	8.1	15.6	28	2.1

Secondly, the implants-inclusion effect is discussed. It has been also reported that for 0.1 MeV Ne ion irradiation on Si_3N_4-film (0.18 μm)/a-SiO_2, there is insignificant composition change and Δn = -1.5% at $6x10^{16}/cm^2$ (dpa=9.4) [9]. As described above, Δn due to the rearrangement effect is -9%. Thus implants-inclusion effect would be Δn ≈ +7.5% at $6x10^{16}/cm^2$. It appears that Δn due to the implants-inclusion follows +7.5(1-exp(-10xFluence))%, here Fluence is in $10^{17}/cm^2$. At present, no data is available for influence of the ion species on the implants-inclusion effect and herein, it is assumed to be independent of ion species. In derivation of the above equation, it is assumed that all implanted Ne are in the film. Since the projected range is comparable with the film thickness, a part of implanted Ne is in the substrate and this should be taken into account for more detail analysis.

The irradiation effects may extend to the a-SiO_2 substrates, since the projected ranges of 0.1 MeV N and Ne (0.18 and 0.15 μm) are comparable with the film thickness (0.2 and 0.18 μm). The increase of the refractive index of a-SiO_2 substrate by *ion irradiation* is ≈ 1% at saturation [17]. Thus, the modification of the refractive index of a-SiO_2 substrates by ion irradiation would be insignificant.

Thirdly, the effect of the composition change is described. It has been reported [14] that for silicon nitride films on a-SiO_2, 10% deficiency in N composition and 5% deficiency in Si composition from the stoichiometry lead to Δn ≈-10% and -3%, respectively. It is assumed that contribution of composition change to Δn linearly scales with the composition deficiency.

Based on the above discussions, the contributions are estimated for Si_3N_4 (0.28 μm)/Si(100) irradiated with 0.1 MeV N, Ne and Ar, and 0.5 MeV N ions. The results are summarized in Table I. For, 0.1 MeV N ion irradiation at 0.92×10^{17} /cm^2, the mean deficiency of the Si composition from the stoichiometry is estimated to be 9% by taking average (approximately a half) of the maximum Si composition deficiency of 18%, which is obtained by assuming the linear dependence of the Si composition deficiency on the fluence and the value of 23% described in §3.2. Similarly, for 0.1 MeV Ar ion irradiation at 1.3×10^{17} /cm^2, the mean deficiency of the Si composition is estimated to be 14% using the RBS result shown in Fig. 3b. Also, the rearrangement effect in this case is the saturation value of -9%. From Table I, one sees that the agreement is poor between the estimated change of the refractive index and the experimental values. A reason for the discrepancy could be the density modification. The density decrease of ~6, 2, 7 and 11% could explain the discrepancy for 0.1 MeV N, Ne, Ar and 0.5 MeV N irradiation [15]. However, the density modification by ion irradiation is not a sole remaining factor for the discrepancy, because the required density modification by ion irradiation does not scale with dpa which is expected to hold for irradiation by ions with ~0.1 MeV.

Furthermore, in the case of 0.5 MeV N ion irradiation, the projected range of 0.66 μm well exceeds the film thickness of 0.28 μm. Thus, ion irradiation effects extend to Si substrate. Modifications of Si substrates may affect the evaluation of the refractive index, because the refractive index of unirradiated Si is employed for the analysis in the ellipsometry. There is no report on the ion irradiation effect on the refractive index of Si in the visible region, except for a report that the refractive index increases by ion irradiation in the infrared region [18].

The refractive index modification by ion irradiation has been discussed phenomenologically in terms of rearrangement, implants-inclusion and composition-change effects (electronic structure modifications). The details of the electronic structure modifications and their influence on the refractive index modifications are to be investigated. In addition, the density modification appears to give significant contribution to the refractive index modification and is to be investigated. As shown in Fig. 4, the nuclear energy deposition has significant depth variation and thus the effect of non-uniform modifications of the refractive index, electronic structures and density are to be included in the analysis.

5. CONCLUSIONS

We have measured the refractive index modification of Si_3N_4 films on Si(100) induced by ion irradiation. It has been observed that the refractive index monotonically decreases with increasing the photon wavelength from 0.4 to 1.7 μm for both unirradiated and ion-irradiated Si_3N_4 films. We have tried to separate each contribution of the electronic structure modifications (rearrangement effect, implants-inclusion effect and composition-change effect) and the density modification to the refractive index modification by ion irradiation.

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