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A study of the charging phenomena during electron irradiation of sintered Si_3N_4

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Abstract

The charging of Si_3N_4 during electron irradiation has been studied using Auger electron spectroscopy (AES). Unlike oxides which monotonously charge up under lasting electron radiation, Si_3N_4 exhibits an abnormal charging behavior, namely it charges up instantaneously to a maximum, then discharges. Ar^+ sputtering damages the surface, which modifies the charging behavior. The charging process on Si_3N_4 will be discussed in terms of the defect states in Si_3N_4 . © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Besides being a high-temperature structural ceramic, silicon nitride (Si_3N_4) is one of the most promising materials with many applications in electronics. To realize the applications, a comprehensive understanding on the basic physical properties of Si_3N_4 is required. Many studies had been devoted to Auger electron spectroscopy (AES) analysis of the irradiation effects of Si_3N_4 films and bulk material [1], and it was found that

charging phenomena occur during AES of Si_3N_4 at primary energies higher than 2 keV [2]. In addition, it had been established that ion beams induce damage on Si_3N_4 , which may modify the charging process. But only limited works dealt with the charging phenomena on Si_3N_4 , and the reported results are not in agreement with each other [1].

For a radiation sensitive material, radiation introduces defects at the surface or in the near surface layer which can modify the composition or the atomic bonds, or both. It is widely accepted that defects, no matter whether they are pre-existing or radiation-induced, can be the cause of the related charging phenomena [3]. In AES the pri-

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mary electron beam serving to excite Auger electrons can modify and charge the surface of the sample. In this paper, we report the use of AES to evaluate the effects of defects on the charging-up of Si_3N_4 by following the variations of the surface composition and by monitoring the efficiency of charge compensation. Environmental AES using inert and reactive gases at very different pressures which affect the charging-up through charge neutralization and passivation of the surface defects, respectively [4], provide an insight into the micro-process of the charging-up.

The charging-up of the Si_3N_4 sample during AES is different from oxides [4] and shows an abnormal dependence on the Ar^+ energy due to sputtering. Following a systematic AES study, the charging phenomena will be discussed in terms of the characteristic of the defect states in Si_3N_4 , such as Si dangling bonds, N dangling bonds and N pair defects. The contribution of the nominal impurities Y, Al and O which dope the Si_3N_4 matrix as sinter-support, is evaluated.

2. Experimental

The Auger electron spectra were recorded with a scanning Auger microprobe with cylindrical mirror analyzer (CMA) operating in the differential mode. The experiments were accomplished with a focused primary electron beam at incidence angles (α) of 30° and 60° with respect to the specimen surface normal. The beam size was about $50\ \mu\text{m}$, and the primary current density varied with the primary energy and incidence angles as indicated in Table 1.

Ar^+ ion sputtering was performed with an ion gun at energies of 1–5 keV and beam current

density of $10\text{--}200\ \mu\text{A}/\text{cm}^2$. The ion beam was set at 60° from the specimen surface normal. The electron and ion beams were aligned on the specimen surface, whereby the ion beam size was about 50 times larger than the electron beam size. Auger spectra were acquired with the sample under a vacuum of 5×10^{-8} Pa. During sputtering the analysis chamber was filled with Ar at a pressure of 3×10^{-5} Pa.

The measured sample was prepared from sintered Si_3N_4 with 15 mass% $\text{Y}_3\text{Al}_5\text{O}_{12}$ dopant. The Si_3N_4 sample was cut into a plate of size $5 \times 3 \times 1\ \text{mm}^3$, and one surface was mechanically polished to give a mirror-like finish. Then it was cleaned in acetone in the ultrasonic bath and rinsed with distilled water. Before the measurements the sample was heated to 300°C in ultra-high vacuum (UHV) to eliminate water. The presence of Al in the sample was detected by AES; Y did not appear in the spectrum; oxygen was found as the main impurity.

3. Results and discussions

At the electron energies ≥ 2 keV and at incidence angles $\leq 30^\circ$, Si_3N_4 charged up “instantaneously” to a maximum, then it discharged. But complete discharging was not observed for primary energies ≥ 3 keV. Fig. 1 shows the typical discharging process from the instantaneous charging potential (U_C), which was determined from the shift of the Auger peaks or the peak edge of secondary electrons, compared to the position of the peaks in the Auger spectrum without charge-up. The data were acquired during the electron bombardment at 5 keV energy and 30° incidence. Table 2 lists the charging potentials af-

Table 1
The primary parameters used in this work

	Primary energies E_p (keV)				
	1	2	3	5	8
Primary current density J_p (10^{-2} A/cm ²)					
$\alpha = 30^\circ$	0.37	0.55	1.08	2.76	68.95
$\alpha = 60^\circ$	0.22	0.32	0.62	1.59	39.80

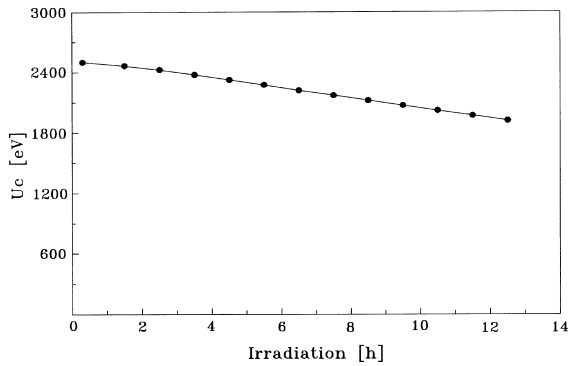


Fig. 1. The charging process of Si₃N₄ under bombardment with 5 keV electrons at 30° incidence.

ter the surface was irradiated with electrons at energies of 3–8 keV and 30° incidence for 1 min and 12 h, respectively. Before each radiation, the sample was sputtered with 2 keV Ar⁺ for 10 min to achieve the same initial surface condition.

Fig. 2 shows the spectra that are registered at 3 keV and 30°. Before the measurement the sample surface had been sputtered with 2 keV Ar⁺ for 10 min. At the beginning of the electron irradiation the surface reached a maximal charging potential of about 65 eV, then it discharged to 15 eV after the electron radiation for 4.5 h. Carbon contamination on the surface could be completely removed through sputtering, but O was always seen. The variation of the ratios of the impurity peak intensities during the 48 h electron radiation is shown in Fig. 3. Some data are missing due to the instantaneous charging-up at the beginning of the radiation. Although there was a pronounced increase of the oxygen and carbon peaks at the beginning, the ratio Si/N remained constant during the whole radiation.

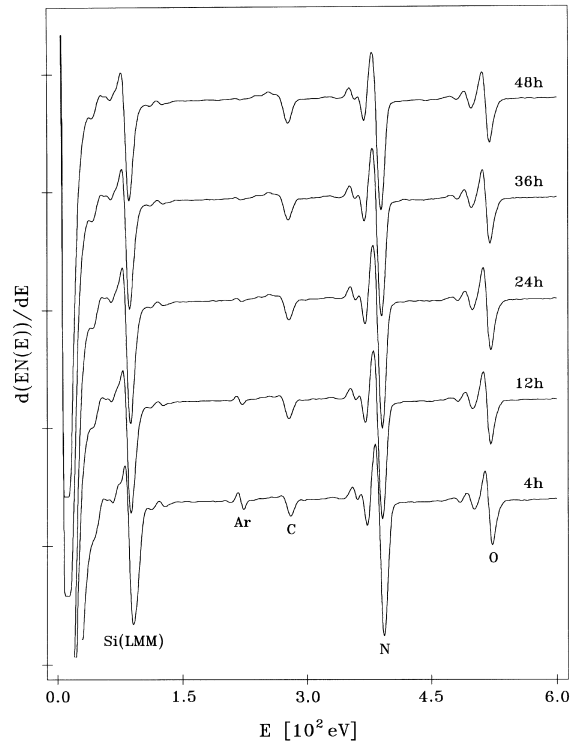


Fig. 2. Auger spectra of Si₃N₄ irradiated with 3 keV electrons at 30° incidence. The irradiation time is indicated on each spectrum.

The charging potential is dependent upon the Ar⁺ energy for sputtering. In the energy range from 1 to 3 keV, ions with higher energy cause higher instantaneous charging during the subsequent electron radiation. Further increasing the ion energy (for example to 4 keV), no such relation had been observed. Fig. 4 shows the charging potentials under continuous impact of 3 keV electrons immediately after sputtering and after

Table 2

The charging potential on Si₃N₄ at beginning and after 12 h of electron radiation at energies ranged from 3 to 8 keV^a

	E _p (keV)					
	3	4	5	6	7	8
Charging (eV) after irradiation						
1 min	100	750	~2500	>2500	>2500	>2500
12 h	20	675	1900	>2500	>2500	>2500

^a Before each measurement the surface was sputtered with 2 keV ions for 10 min.

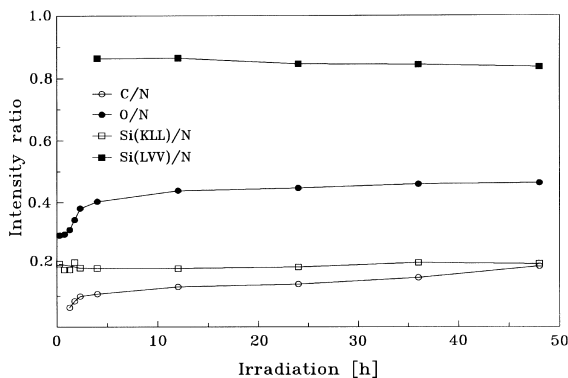


Fig. 3. Variations of the peak intensity ratios during 3 keV electron irradiation ($\alpha = 0^\circ$). Before the measurement the surface has been sputtered with 2 keV Ar^+ for 10 min.

12 h, respectively. To reach saturated charging potential, it needs longer time for higher ion energies.

In order to investigate the charging phenomena, AES had been performed in Ar, He, O_2 and N_2 environments. Ar and He gases at pressures up to 1.3×10^{-2} Pa showed hardly any reduction of charging. For the same purpose, O_2 and N_2 environments was kept at a pressure below 6×10^{-6} Pa. This N_2 environment also could not obviously reduce the charging potential. But O_2 was more efficient compared with the other gases, though it contaminates the sample surface.

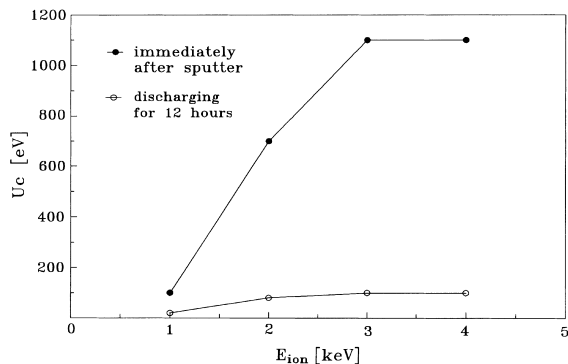


Fig. 4. Sputtering effect on the charging potential of Si_3N_4 as the function of Ar^+ energy. The upper curve displays the charging potentials at the beginning of electron irradiation; the lower curve shows the charging potential after the surface had been irradiated by the electrons for 12 h ($E_p = 3$ keV, $\alpha = 30^\circ$).

The effect of specimen heating on the charging phenomena has been examined. Heating the sample up to 600°C reduced the charging to some extent, but a combination of specimen heating and O_2 environment (6×10^{-6} Pa) is necessary to achieve a more significant reduction in the charging potential.

Based on factor analysis of AES spectra, Bender et al. [1] determined that it needs electron dose (3 keV) of $2\text{--}7 \times 10^4$ C/cm² to damage low pressure CVD (LPCVD) and plasma enhanced CVD (PECVD) silicon nitride films. Compared to Si_3N_4 films, bulk Si_3N_4 should be more radiation resistant. The electron beam damage on Si_3N_4 is not evident in our results. This agrees with the results reported by Pantano and Madey [5].

As Figs. 2 and 3 indicated, the adsorption of O and C was occurring mainly at the beginning of the electron irradiation. To get a lateral profile of oxygen contamination caused by electron irradiation, the (2 keV Ar^+) sputtered surface was first bombarded for 48 h with a defocused electron beam at 4 keV (0.5 mm diameter). Then measurements were made across the irradiated zone with a focused electron beam at 1 keV energy, at which no charging appeared. Fig. 5 shows the point by point measurement of oxygen across the irradiated zone. The maximal oxygen intensity does not lie in the center of the irradiated zone, but outside it. Only far from the irradiated zone there is uniform oxygen coverage. Similar results had been reported by Verhoeven et al. [6]. They exposed the CO pre-covered Ni(1 0 0) surface to an intensive electron beam, and they explained the observed phenomenon by the diffusion of oxygen following the dissociation of CO. We believe that the big oxygen peak is mainly due to adsorption of the residual gas. In the irradiated region, where electron stimulated adsorption (ESA) and electron stimulated desorption (ESD) compensated each other, the resulted oxygen contamination cannot be as high as outside, where the oxygen adsorption is enhanced due to absent of ESD.

The gas environments could not eliminate the charging-up on Si_3N_4 . In combination with the fact that Si_3N_4 is resistant to the electron radiation, we conclude that the charging-up on Si_3N_4 is a bulk effect, and that the electron traps should be

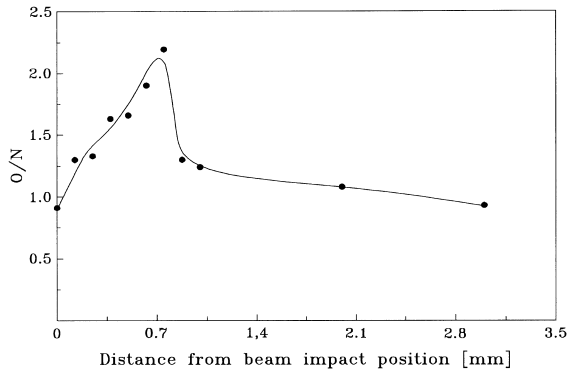


Fig. 5. Lateral distribution of the oxygen contamination across the irradiated zone. The zone had been irradiated with a defocused 4 keV electron beam for 48 h (beam size ~ 0.5 mm, $E_p = 1$ keV, $\alpha = 30^\circ$).

intrinsic defect. It is known that Si dangling bonds (Si-DB $:= \text{Si}^\cdot$) in Si_3N_4 are electron traps which are employed as the memory medium in non-volatile metal–nitride-oxide-semiconductor (MNOS) devices [7–9]. Si-DBs act as memory traps because of their amphoteric nature, depth and energy aligned with the gap of bulk Si [7]. Although trapping and detrapping in MNOS is realizable by inverting the device bias [10–12], in bulk Si_3N_4 discharging of the charged Si-DB is not easy. The activation energy of the trapped electrons is determined by the depth of the energy level of Si-DB with respect to the lower edge of the conduction band, which is about 3 eV [13].

N dangling bonds (N-DB $:= \text{N}^\cdot$) and N pair defects (N-PD $:= \text{N}-\text{N}^\cdot$) are also electron traps, since both give energy states in the band gap and are singly occupied when they are neutral [14,15]. In CVD- Si_3N_4 , a Si-DB density of $10^{19}/\text{cm}^3$ had been estimated [7]. In PD- $\text{Si}_3\text{N}_4:\text{H}$, the N-DB concentration up to $1 \times 10^{18}/\text{cm}^3$ had been measured [13]. N-PDs in a density range of 10^{15} – $10^{16}/\text{cm}^3$ had been determined in GD- Si_3N_4 (glow-discharged decomposition) [16]. Unlike a- SiO_2 which can be stoichiometric and pure, sintered Si_3N_4 is normally defective. Fig. 6 is the schematic diagram of the energy levels of the intrinsic defects in Si_3N_4 [14,15].

Unlike oxides, which charge monotonously under electron radiation [17,18], the abnormal

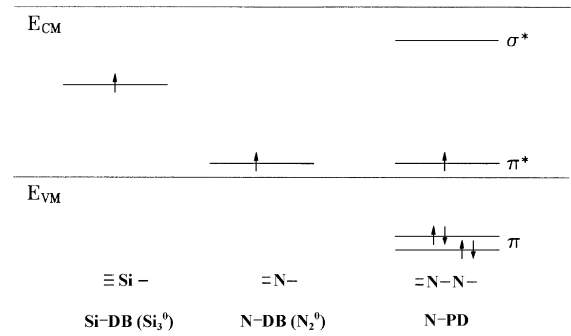


Fig. 6. Schematic diagram of the energy levels of the intrinsic defects in Si_3N_4 . E_{CM} and E_{VM} are the energies at the lower edge of the conducting band and the upper edge of the valance band of Si_3N_4 , respectively.

charging behavior of Si_3N_4 can result from the defect states. It has been confirmed that the Si-DBs are energetically favorable as electron traps [19,20]. Thus, neutral and charged defects like Si_3^0 , Si_3^- , Si_3^+ , N_2^0 and N_2^- are in equilibrium, which depends on the primary parameters. Simultaneously, hopping conduction between defect centers is possible [10,21], especially among Si_3^0 , Si_3^- and Si_3^+ , which lie energetically side by side [7,14].

The effect of Ar^+ sputter on charging-up of Si_3N_4 can be understood through the presence of irradiation effects. Ar^+ breaks the regular Si–N bonds, which enables the concentrations of the Si-DB and N-DB in the top layer of the sample to increase. Preferential sputtering of N from Si_3N_4 has been confirmed [1,22–25]. Bender et al. found that the level at which the damage saturated was independent on the Ar^+ energy in the range of 1.5–4 keV [1], while Chao et al. reported that low energy Ar^+ ion (0.5–1.5 eV) are more effective than higher energy (3–4 keV) in damaging Si_3N_4 [26]. Our results show a dependence of charging-up on the ion energy in the range of 1–3 keV. Sputtering with higher Ar^+ energy causes stronger charging-up (Fig. 4). The sputter yield of 4 keV Ar^+ is about 30% higher than that of 1.5 keV Ar^+ [1], and the penetration depth and the final defect densities are different as well. The maximum charging potential strongly increased with Ar^+ energy up to 3 keV; further raising the Ar^+ energy did not lead to an increase of the charging potential. Both pre-exist-

ing and radiation-induced defects cause charging [2]. Simultaneously, the defects assist the hopping conduction. Thus, Ar^+ energies higher than 4 keV does not cause more charging.

The annealing behavior of the spin densities of Si-DB, N-DB and N-PD in a- $\text{Si}_3\text{N}_4\text{:H}$ has been studied by Yan et al. [16]. They found that the temperature dependence of these defects densities is similar to those of E' , non-bridge oxygen (NBO) and peroxy radical (PR) in a- SiO_2 [27,28]. In a- $\text{Si}_3\text{N}_4\text{:H}$, the concentration of Si-DB and N-DB was about $5 \times 10^{17}/\text{cm}^3$ at room temperature and dropped to about $2 \times 10^{15}/\text{cm}^3$ by 400°C , whereby N-PD reached a maximum [16]. To reduce the N-PD density to below $10^{15}/\text{cm}^3$, temperatures higher than 500°C are required [16]. Our results can be understood following the annealing behavior of these defects.

The studied samples are doped with 15 mass% $\text{Y}_3\text{Al}_5\text{O}_{12}$, which corresponds to impurity concentrations of 5.45 at.% O, 2.27 at.% Al and 1.36 at.% Y. There is neither theoretic nor experimental results, which are available to evaluate the effects of these impurities on the charging-up of Si_3N_4 . It is clear that the O_2 environment can passive the defects on the surface, such as the Si-DBs and N deficit centers formed by Ar^+ sputtering [29]. Therefore, an oxygen environment is efficient in reducing the charging potential. This fact may lead to the conclusion that these impurities themselves are not the primary cause for the charging-up of the Si_3N_4 sample.

4. Conclusions

Sintered Si_3N_4 shows pronounced charging under electron bombardment. The maximal charging potential is instantaneously achieved, then it is followed by a slow and limited discharge. The impurities Y, Al and O could not be the primary causes for this abnormal charging behavior. Instead, Si-DB, N-DB and N-PD, which exist at high concentration in bulk Si_3N_4 are believed to be the electron traps. It is proposed that the discharging observed after achievement of the maximal charging potential could be due to the reduced density of the dangling bonds on the surface due to

passivation from residual gas and due to hopping conduction associated with the amphoteric defects.

Although the charging process on Si_3N_4 is a bulk effect, ion sputtering can modify the charging phenomena. Energetic ions damage the surface and increase the density of dangling bonds, which cause stronger charging, and enhance hopping conductivity as well. Thus, an abnormal charging phenomenon following ion energies is observed.

Charge compensation could not be expected by specimen heating lower than 600°C . O_2 environment passives the defect centers on the surface, which leads to a reduction of the charge potential, especially in cooperation with specimen heating.

Acknowledgements

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