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Novel oxidation process of hydrogenated amorphous silicon utilizing nitrous oxide plasma

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A novel oxidation process in hydrogenated amorphous silicon (*a*-Si:H) using nitrous oxide (N₂O) plasma was studied in detail for the first time. The N₂O-plasma oxidized *a*-Si:H has an excellent interface whose interfacial defect density is largely reduced compared with the O₂-plasma oxidized *a*-Si:H. It was elucidated that this oxide layer has almost stoichiometric composition and contains a small amount of N piling up at the interface between the oxide layer and *a*-Si:H layer. It also turned out that this process has less ion damage than the O₂-plasma oxidation process. The reason for the reduction of the interfacial defect density is attributed to the presence of N at the interface and/or less ion damage in this process.

In recent years, nitrous oxide (N₂O) has been employed as an excellent oxidizing agent. For instance, the silicon dioxide (SiO₂) films for fabrication of metal-oxide-semiconductor (MOS) structure in III-V compound semiconductors were prepared by photolysis of disilane (Si₂H₆) with N₂O.¹ It was also reported that SiO₂ films were prepared by plasma-enhanced chemical vapor deposition (PECVD) using a gaseous mixture of silane (SiH₄) and N₂O.² It became apparent that the step coverage in SiO₂ prepared by the downstream microwave PECVD method using a gaseous mixture of tetraethoxysilane (TEOS) and N₂O is quite improved.³ In our group it was also found that in the pulsed laser ablation technique utilizing ArF excimer laser, N₂O ambient enhances the *c*-axis orientation for the Ba₂YCu₃O_x superconducting thin films on crystalline Si substrates⁴ and the formation of the perovskite structure of Pb(Zr_{0.52}Ti_{0.48})O₃ (PZT) ferroelectric thin films on *r*-plane sapphire substrates.⁵ Thus, the processes using N₂O are of great interest, and it is of urgent necessity to elucidate these processes. In this study, a novel oxidation process of hydrogenated amorphous silicon (*a*-Si:H) using N₂O plasma has been developed. It was previously reported that this process gives a low interfacial defect density.⁶ We have investigated this process as an oxidation method of *a*-Si:H in detail, and clarified the origin of the reduction in the defect density for the first time.

The sample films were prepared in two stages. In the first place, the *a*-Si:H layer was deposited by the PECVD method using SiH₄ without dilution. After the deposition of the *a*-Si:H layer of the thickness of about 2000 Å, SiH₄ was completely exhausted and N₂O was immediately introduced to the preparation chamber. Subsequently plasma-enhanced oxidation was performed utilizing N₂O plasma, and also O₂ plasma for comparison. Throughout both stages, substrate temperature was kept at 300 °C. In the plasma-enhanced oxidation process, rf (13.56 MHz) power density and total pressure were kept at 0.24 W/cm² and 18 Pa, respectively. The oxidation process was monitored by optical emission spectroscopy (OES). The sample films were evaluated using electron spin resonance (ESR)

measurements, x-ray photoelectron spectroscopy (XPS), and Auger electron spectroscopy (AES). ESR measurements were done at room temperature using the sample formed on the fused quartz substrates. XPS and AES measurements were performed under the vacuum less than 2×10^{-8} Pa for the samples formed on the *n*⁺-type Si(111) substrates whose resistivity is the order of 10⁻³ Ω cm to avoid the effect of the chargeup.

The neutral defect density per area obtained by ESR measurements is shown in Table I. The neutral defects created during the plasma-enhanced oxidation is thought to exist in the *a*-Si:H layer because the *g*-value for these defects is about 2.0055. From Table I, N₂O-plasma oxidized *a*-Si:H has the neutral defect density whose value is almost equal to that observed in *a*-Si:H before plasma oxidation. On the other hand, in the case of the O₂-plasma oxidation, a large increase in the neutral defect density is observed. It is appropriate to consider that these defects exist near the interface in the *a*-Si:H layer by forming the oxide layer. It is worth noting that the remarkable reduction in the neutral defect density is accomplished using N₂O plasma. Therefore in this study, the N₂O-plasma oxidation is investigated in detail.

Figure 1 shows the oxidation time dependence of the oxide thickness. The oxide thickness was calculated using the intensity ratio of Si 2*p* spectrum originated from SiO₂ to that from *a*-Si:H. From Fig. 1, it is clarified that the N₂O-plasma oxidation rapidly progresses in the early stage, and then the oxide thickness saturates for about 20 min at about 50 Å. The oxide thickness formed by O₂ plasma for 20 min is also shown in Fig. 1 for comparison. The following results were obtained for the sample after N₂O-plasma oxidation for 20 min. The spectrum of Si 2*p* obtained by XPS for the N₂O-plasma oxidized *a*-Si:H is shown in Fig. 2. In this figure, the spectrum observed in *a*-Si:H is also shown for comparison. It was revealed that the N₂O-plasma oxidized *a*-Si:H has almost stoichiometric composition, namely SiO₂, from the fact that the signal due to Si—O bonding shown by a circular symbol is observed at 103.1 eV in Fig. 2. A similar result was also obtained by

TABLE I. The neutral defect density in α -Si:H films after and before plasma-enhanced oxidation treatments.

Process	Neutral defect density ($\times 10^{12} \text{ cm}^{-2}$)
α -Si:H after N_2O -plasma oxidation	1.6
α -Si:H after O_2 -plasma oxidation	6.1
α -Si:H before plasma oxidation (kept in vacuum)	1.5

AES. The signal obviously observed at 98.7 eV in the N_2O -plasma oxidized α -Si:H, shown by a triangular symbol in Fig. 2, is originated from the α -Si:H layer. The wrong interpretation from this signal that the oxide film separates into Si and SiO_2 is denied because the signal due to α -Si:H was hardly observed by AES. This difference results from the fact that AES is more sensitive to the surface than XPS. The energy shift in the signal due to α -Si:H, observed in Fig. 2, is thought to be not essential but originated from the unavoidable chargeup for the sample with an oxide. Although the oxide formed utilizing N_2O plasma is SiO_2 as mentioned above, the XPS signal separation using Gaussian suggests that this oxide film has a small amount of suboxide SiO_x ($x < 2$). It was also elucidated by XPS that the process is not pyrolysis but plasma process because no discharge of N_2O induces no Si $2p$ spectra originated from Si—O bonding.

It also turned out using XPS that a small amount of N is contained in these oxide films formed by N_2O plasma. It was confirmed that this N does not have its origin in the contamination during the oxidation but in the decomposition of N_2O because no signal due to N is observed in O_2 -plasma oxidized α -Si:H. Therefore the depth profile of N was investigated using the angle-dependent XPS (ADXPS). This method is excellent because it elucidates the depth profile without destroying the samples in contrast with XPS or AES combined with the ion sputtering or secondary ion mass spectrometry (SIMS). Accordingly it is possible by utilizing the ADXPS method to avoid the mixture of the constituent elements or the preferential

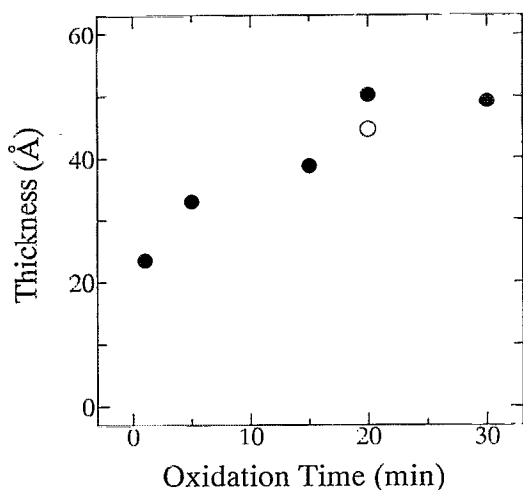


FIG. 1. Oxidation time dependence of the oxide thickness formed using N_2O plasma (●) and O_2 plasma (○).

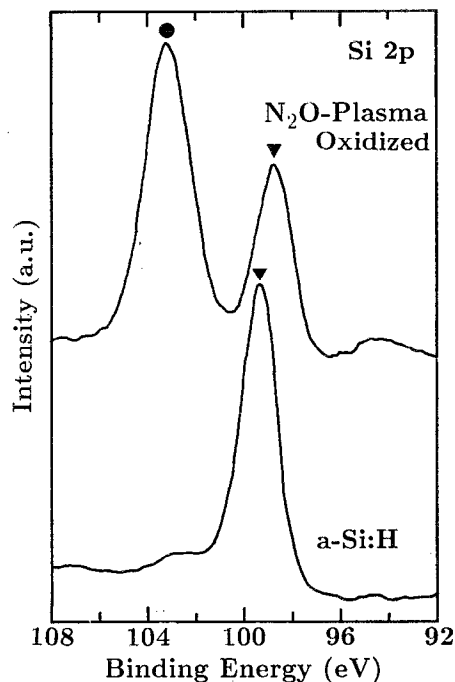


FIG. 2. XPS spectra in Si $2p$ observed in α -Si:H and N_2O -plasma oxidized α -Si:H. Circular and triangular symbols show the spectra due to SiO_2 and α -Si:H, respectively.

sputtering which have a bad influence upon the analysis. Figure 3 shows the dependence of the photoelectron intensity of the signals due to Si $2p$, O $1s$, and N $1s$ on the change of the photoelectron takeoff angle. The values are normalized to those observed at 90° , and the division of the spectrum originated from Si $2p$ into the signals due to α -Si:H and SiO_2 is performed for analysis. It is remarkable that the signal due to N $1s$ is attenuated faster than that due to O $1s$ or Si $2p$ originated from SiO_2 . This experimental fact shows that N is not distributed all over the oxide layer but piles up near the interface between oxide and α -Si:H. Such a phenomenon was reported in thin SiO_2 films

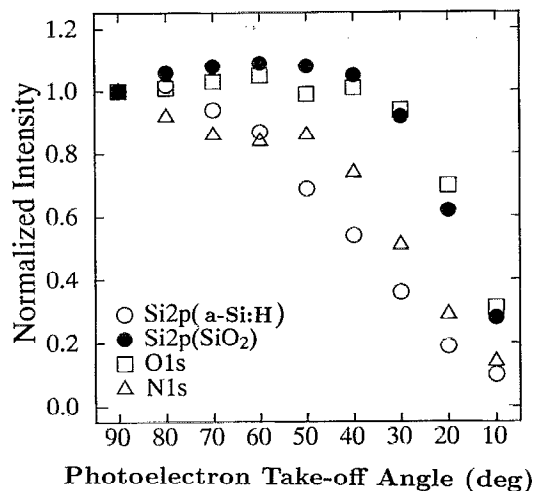


FIG. 3. Photoelectron takeoff angle dependence of the photoelectron intensity. Each value is normalized to that observed at 90° in the takeoff angle.

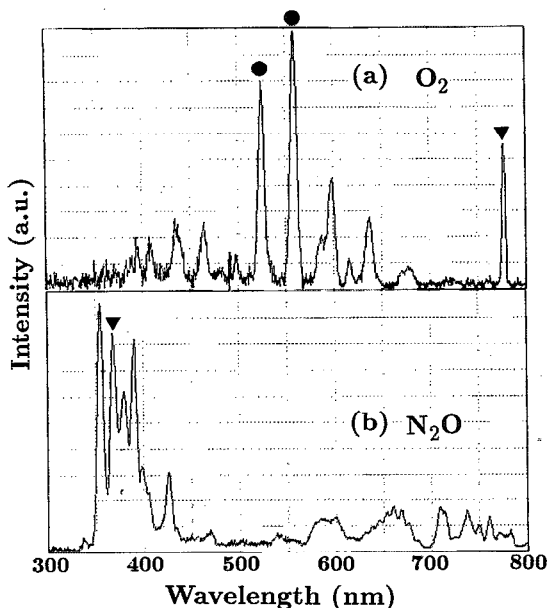


FIG. 4. OES spectra observed in (a) O_2 plasma and (b) N_2O plasma.

formed by multiple rapid thermal processing (RTP) on Si(100) using O_2 and N_2O as reactants.⁷ It is estimated from the results of ADXPS that the silicon oxynitride (SiO_xN_y) layer of thickness of about 4 Å exists at the interface, and its composition is $SiO_{1.7}N_{0.3}$.

The N_2O - and O_2 -plasma emission was observed by OES. Figures 4(a) and 4(b) show the spectra obtained from O_2 plasma and N_2O plasma, respectively. In the O_2 plasma, the emission line due to atomic oxygen ($3p \rightarrow 3s$)⁸ is observed at 777.4 nm as shown by a triangular symbol, however, the emission lines due to O_2^+ ion⁸ observed between 500 and 700 nm are dominant as shown by circular symbols. On the other hand, in the N_2O plasma the emission lines due to O_2^+ ion are scarcely observed. The emission line observed at 369.2 nm shown by a triangular symbol is due to the atomic oxygen ($5p \rightarrow 3s$).⁹ This fact indicates that the N_2O -plasma oxidation progresses dominantly by atomic oxygen and gives little plasma damage due to O_2^+ ions compared with the O_2 -plasma oxidation.

Two reasons are proposed for the reduction of the interfacial neutral defect density in the case of the N_2O -plasma oxidation. One reason is that N piling up at the interface plays an important role in reducing the creation of defects. It is easy to suppose that the strong Si—N bonds are substituted for the weak bonds existing at the interface.⁷ The other reason is that the utilization of N_2O plasma remarkably reduces the ion bombardment during the oxidation compared with the case using O_2 plasma. In order to test the effect of the ion bombardment, the interface between oxide and α -Si:H was observed using stylus profilometry. In this experiment, the oxide layer was previously removed by dipping in hydrofluoric acid. From this experiment, it is revealed that the interfacial morphology in N_2O -plasma oxidized sample is smooth, showing less than 20 Å undulation. On the other hand, the O_2 -plasma oxidized interface is rough and has undulation of about 30 Å. Therefore it is suggested that the effect of the ion bombardment is larger for the O_2 -plasma oxidation than for the N_2O -plasma oxidation. Under the present conditions, both the little ion bombardment and the role of N at the interface are proposed as the reason for the less interfacial defects utilizing N_2O -plasma oxidation.

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