Jpn. J. Appl. Phys. Vol. 35 (1996) pp. 2614–2618
Part 1, No. 5A, May 1996

Interface Electronic Properties between Silicon and Silicon Nitride Deposited by Direct Photochemical Vapor Deposition

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(Received November 24,1995; revised manuscript received January 16, 1996; accepted for publication February 15, 1996)

Interface electronic properties of silicon nitride (SiN_x)/crystalline silicon (c-Si) are studied. The interface electronic properties are improved by changing NH_3/SiH_4 flow ratios (F_{NH3}/F_{SiH4}) of a thin SiN_x layer ($\simeq$ 6 nm in thickness) between c-Si and a thick SiN_x layer ($\simeq$ 65 nm) deposited with F_{NH3}/F_{SiH4} = 30, where both SiN_x layers are formed by direct photochemical vapor deposition (photo-CVD). In the case of F_{NH3}/F_{SiH4} = 120, the minimum interface-trap density and hysteresis obtained from the capacitance-voltage (C–V) characteristics of Al/thick SiN_x/thin SiN_x/c-Si diodes are 3×10^{10} cm$^{-2}\cdot$eV^{-1} and 0.1 V, respectively. In the deposition of thin SiN_x, the interface electronic properties are degraded by exposing Si_xH_y or N_xH_y species to a c-Si surface, where these species are produced by photodecomposition of NH_3/SiH_4 gas mixtures. Injected carriers, which cause hysteresis of the C–V characteristics, are discussed in terms of the barrier height for tunneling and the number of interface traps.

KEYWORDS: silicon nitride, photo-CVD, MIS, interface traps, hysteresis, flatband voltage shift

1. Introduction

Silicon nitride (SiN_x) has been an attractive material for use in LSI as a final protective film and a diffusion barrier, because of its high impermeability to water or impurities.[1,2] SiN_x has been deposited by plasma chemical vapor deposition (plasma CVD) of NH_3/SiH_4 gas mixtures at a low temperature ($\sim$ 350°C). Recently, SiN_x has been used as a gate insulator in amorphous thin-film transistors.[3] However, ions produced in the plasma bombard a semiconductor surface, which damages insulator/semiconductor interfaces.

SiN_x can be deposited by photo-CVD without ion bombardment at a low temperature. By direct photo-CVD with an NH_3/SiH_4 gas flow ratio (F_{NH3}/F_{SiH4}) of 30,[4] the resistivity of SiN_x reached 5×10^{16} $\Omega\cdot$cm which was higher by two orders of magnitude than that deposited by plasma CVD. In SiN_x deposited by photo-CVD at 500°C, the refractive index and the dielectric constant were 1.95 and around 6, respectively, and these values approached those of SiN_x deposited by thermal CVD at 700°C.[5,6] SiN_x deposited by direct photo-CVD, therefore, is one of the candidates for gate insulators.

In order to study electronic properties originating only from SiN_x/Si interfaces, metal/SiN_x/crystalline-silicon (c-Si) diodes are investigated. Yoshimoto *et al.*[4] reported electronic properties of these diodes fabricated by direct photo-CVD: a flatband voltage shift (ΔV_{FB}) of 0.02 V, hysteresis (ΔV_h) of 0.14 V, and a minimum interface-trap density of 3×10^{10} cm$^{-2}\cdot$eV^{-1} were obtained from the 1 MHz capacitance–voltage (C–V) characteristics. However, these good properties were obtained in samples prepared without removal of native oxide on c-Si before SiN_x deposition.

Hydrofluoric acid (HF) treatment (removal of native oxide on c-Si) is always done in fabrication processes of field-effect transistors (FETs). In this study, therefore, c-Si wafers soaked in a solution of HF are used. Before the deposition of a thick SiN_x film (about 65 nm) at 500°C with F_{NH3}/F_{SiH4} = 30, a thin SiN_x layer (about 6 nm) is deposited at 500 °C with various F_{NH3}/F_{SiH4}. The 1 MHz C–V characteristics of the metal-insulator-semiconductor (MIS) diodes are measured in order to study electronic properties at the interfaces. By changing the deposition conditions (F_{NH3}/F_{SiH4}, the order of gas supply, etc.) for thin SiN_x, the effects of chemical species in the vapor phase on the interface properties are studied. The origin of hysteresis in the C–V characteristics is discussed in terms of N/Si atomic ratios in thin SiN_x and the number of interface traps.

2. Experimental

SiN_x was deposited at 500°C by direct photo-CVD using NH_3 and SiH_4 gas mixtures without mercury (Hg) sensitization. A low-pressure Hg lamp with an input power of 400 W was used as the light source. Figure 1 shows a reaction chamber (697 mm $\times$ 190 mm $\times$ 50 mm) with a window made of quartz (165 mm$^\phi$) which is transparent for 185 and 254 nm mercury lines. N_2 was introduced with a flow rate of 800 sccm to the upper side of the chamber to prevent the deposition of SiN_x on the window. The total pressure was kept at 7.5 Torr.

Figure 2 shows a schematic of MIS structure. Before SiN_x deposition, an n-type (100) c-Si (n c-Si) wafer with a donor concentration (N_d) of 1.5×10^{15} cm^{-3} was soaked in a solution of HF to remove native oxide on c-Si, followed by rinsing in deionized water. A c-Si surface with-

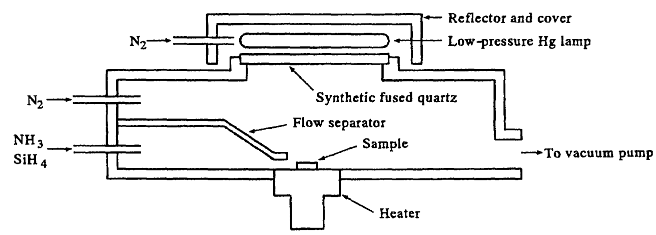

Fig. 1. Schematic of reaction chamber.

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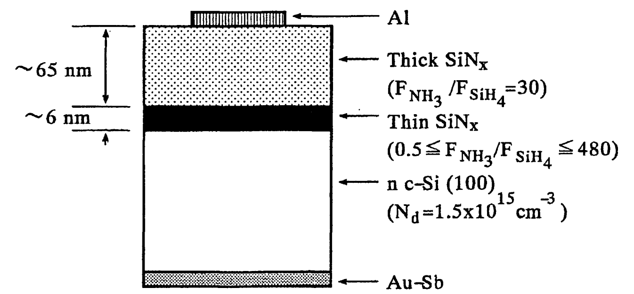

Fig. 2. Metal-insulator-semiconductor structure.

out native oxide is hydrophobic. As soon as the c-Si surface became hydrophobic, it was transferred into the chamber.

A thin SiN_x layer with thickness around 6 nm was deposited with $0.5 \leq F_{NH3}/F_{SiH4} \leq 480$. SiH_4 was introduced to the chamber before NH_3 was supplied. This order of gas supply will be discussed in detail in §3.1.1.

A thick SiN_x layer of around 65 nm was subsequently deposited with $F_{NH3}/F_{SiH4} = 30$. The flow rates of NH_3 and SiH_4 were 45 and 1.5 sccm, respectively. The thick SiN_x has favorable properties as a gate insulator. The refractive index determined by ellipsometry was 1.94, and the dielectric constant estimated from the capacitance at 1 MHz was around 7.0. The resistivity was about $5 \times 10^{16}\,\Omega\cdot$cm below an electric field of 3 MV/cm, and the breakdown field was around 8 MV/cm.

In order to obtain an ohmic contact with n c-Si, Au–Sb (0.5% Sb in Au) was evaporated onto the HF-treated back of c-Si, followed by alloying at 400°C for 1 min in Ar. Then, Al was evaporated on the SiN_x film with an area of 1.96×10^{-3} cm^2. The 1 MHz C–V characteristics of MIS diodes were measured at room temperature in the dark using a Hewlett-Packard 4192A impedance analyzer, where the ramp speed of bias voltages was 0.04 V/s. The interface-trap density (D_{it}) was estimated from the C–V characteristics by the Terman method.[7]

3. Results and Discussion

3.1 *Interface traps*

Figure 3 shows the relationship between minimum D_{it} and F_{NH3}/F_{SiH4} for the deposition of thin SiN_x, where minimum D_{it} is the value of the minimum interface-trap density in its energy distribution within the Si band gap. The minimum D_{it} decreased with an increase in $F_{NH3}/F_{SiH4} \leq 120$, while it increased rapidly with $F_{NH3}/F_{SiH4} > 120$. In the case of $F_{NH3}/F_{SiH4} = 120$, the minimum D_{it} reached around $3 \times 10^{10}\,\mathrm{cm^{-2}\cdot eV^{-1}}$.

Let us consider the effects of chemical species in the vapor phase on interface traps. In the direct photo-CVD system with a low-pressure Hg lamp using NH_3 and SiH_4 mixtures, NH_3 absorbs 185 nm light strongly, and is dissociated almost exclusively into NH_2 and H radicals.[8] On the other hand, SiH_4 is not decomposed by 185 and 254 nm mercury lines.[9] The radicals formed from NH_3 decomposition react with SiH_4, resulting in the production of other radicals and molecules such as silyl radicals (SiH_3), disilane (Si_2H_6), silylamine (SiH_3NH_2), and diaminosilane [$SiH_2(NH_2)_2$].[4,10] In order to investigate the role of chemical species, the species produced during the photo-CVD are classified into three groups: N_xH_y, Si_xH_y, and $Si_xN_yH_z$.

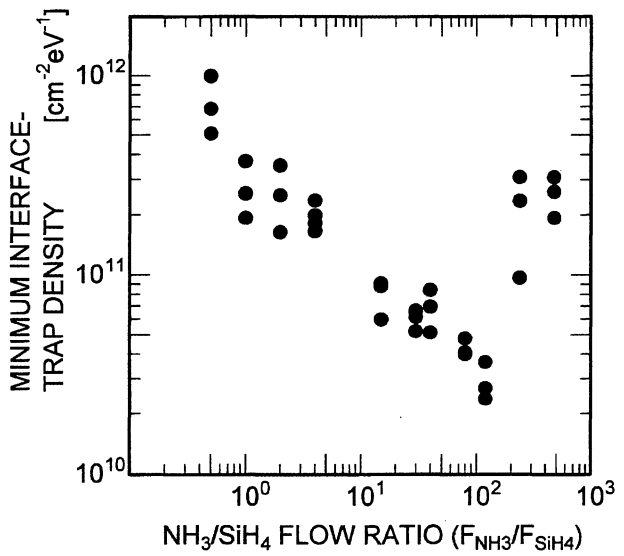

Fig. 3. Relationship between minimum interface-trap density and NH_3/SiH_4 flow ratio for thin SiN_x.

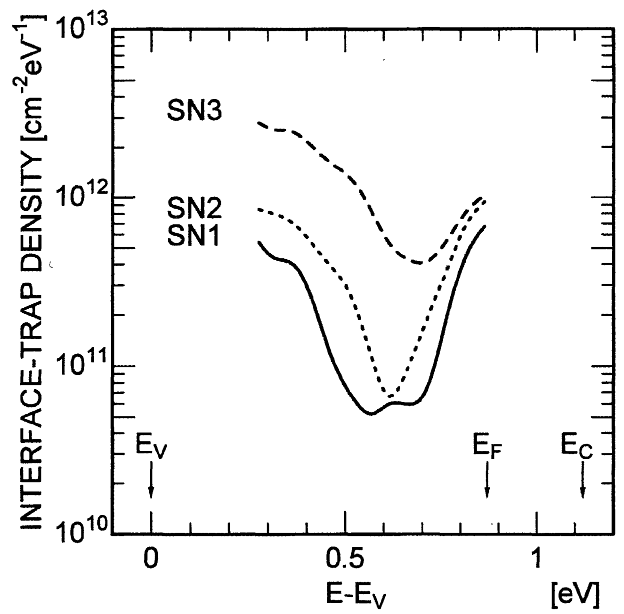

Fig. 4. Dependence of interface-trap density on the order of gas supply. In SN1, SiH_4 was introduced for 30 s before both NH_3 and SiH_4 were supplied, and in SN2 or SN3, NH_3 was supplied for 30 s or 30 min before NH_3 and SiH_4 were supplied.

3.1.1 *Effects of N_xH_y species*

In order to understand the effect of N_xH_y species on D_{it}, the order of gas supply was first examined using MIS diodes without thin SiN_x layers. The interface-trap-density distribution in the energy gap is shown in Fig. 4, where E_F, E_C, and E_V represent the energies of the Fermi level, the bottom of the conduction band, and the top of the valence band in c-Si, respectively. In the sample of SN1, only SiH_4 was supplied for 30 s before both NH_3 and SiH_4 were supplied into the chamber. In SN2, on the other hand, only NH_3 was supplied for 30 s before NH_3

and SiH_4 were supplied into the chamber, indicating that the HF-treated c-Si surface was exposed for 30 s to N_xH_y species formed from the photodecomposition of NH_3. In SN3, the HF-treated c-Si surface was exposed to N_xH_y species for 30 min before the SiN_x film was deposited.

In the case of SN1, as soon as N_xH_y species are produced by the photodecomposition of NH_3, N_xH_y species can react with SiH_4, because SiH_4 is already present when NH_3 is introduced into the chamber. In SN2 and SN3, on the other hand, N_xH_y species cannot react with SiH_4 until SiH_4 is supplied. In SN1, therefore, the effect of N_xH_y species on the c-Si surface is less than those in SN2 and SN3. Since D_{it} in SN1 is lower over the whole energy range than those in the other samples, N_xH_y species are considered to degrade the electronic properties at the SiN_x/c-Si interfaces. Therefore, SiH_4 should be introduced to the chamber before NH_3 is supplied.

Since the effect of N_xH_y species has been explained, the minimum D_{it} of the MIS diodes (Al/thick SiN_x/thin SiN_x/n c-Si), which is shown in Fig. 3, is considered again. In the case of $F_{NH3}/F_{SiH4} > 120$, the minimum D_{it} was much higher than that in the case of $F_{NH3}/F_{SiH4} = 120$, and quite similar to that of SN3 in which the c-Si surface was exposed to N_xH_y species for a long time (Fig. 4). This suggests that, in the case of $F_{NH3}/F_{SiH4} > 120$, N_xH_y species exist in the chamber since the amount of SiH_4 is too small to react with all N_xH_y species. Therefore, the remaining N_xH_y species are considered to degrade the interface properties. In the case of $F_{NH3}/F_{SiH4} = 120$, since the minimum D_{it} was much lower than that in the case of $F_{NH3}/F_{SiH4} > 120$, N_xH_y species react almost exclusively with SiH_4, and may not exist in the chamber.

3.1.2 *Effects of Si_xH_y species*

Figure 5 exhibits the relationship between the N/Si atomic ratio in films and F_{NH3}/F_{SiH4}, where the N/Si atomic ratio was measured by means of Auger electron spectrometry (AES) using SiN_x films (between 30 and 100 nm thick) deposited with $0.5 \leq F_{NH3}/F_{SiH4} \leq 480$.

The N/Si atomic ratio was about 1.33 in the case of $15 \leq F_{NH3}/F_{SiH4} \leq 240$, indicating that the films are stoichiometric (Si_3N_4). In the case of $F_{NH3}/F_{SiH4} < 15$, on the other hand, these films are Si-rich since the ratio was smaller than 1.33. This suggests that, in the case of $F_{NH3}/F_{SiH4} < 15$, a large number of Si_xH_y species takes part in the SiN_x deposition as F_{NH3}/F_{SiH4} decreases.

Since the minimum D_{it} increased with decreasing F_{NH3}/F_{SiH4} in Fig. 3, Si_xH_y species are considered to affect the interface properties adversely. Therefore, the surface of HF-treated c-Si should not be exposed to Si_xH_y species.

3.1.3 *Effects of $Si_xN_yH_z$ species*

By quadrupole mass spectroscopic analysis (QMA) of the photo-CVD system with NH_3/SiH_4 gas mixtures, $Si_xN_yH_z$ species increased with increasing F_{NH3}/F_{SiH4},[11] which coincides with results obtained by Beach and Jasinski.[10] Because the minimum D_{it} is found to decrease not only with an increase in the number of $Si_xN_yH_z$ species but also with a decrease in the number of Si_xH_y or N_xH_y species, it is considered that SiN_x films should be deposited on c-Si only from $Si_xN_yH_z$ species.

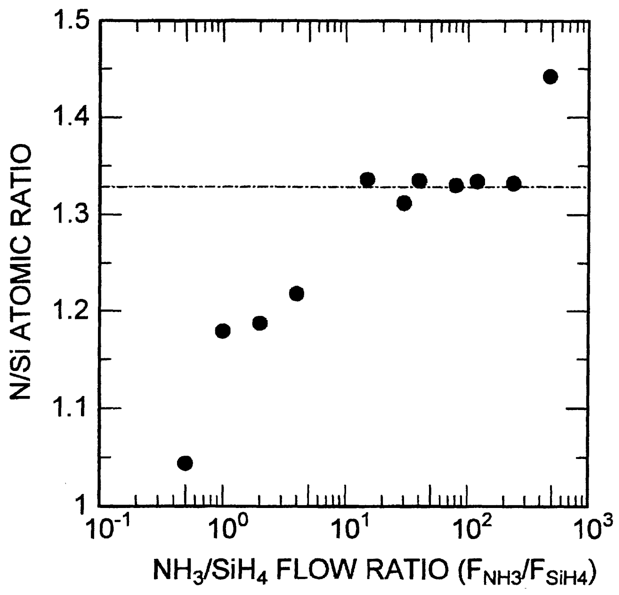

Fig. 5. Relationship between N/Si atomic ratio in thin SiN_x and NH_3/SiH_4 flow ratio. The dot-dashed line represents the stoichiometric value (N/Si atomic ratio is 1.33).

By time-resolved QMA, Si_2NH_7 or SiN_3H_7 (AMU 77) was found to be produced through $SiNH_5$(AMU 47), and the signal at AMU 44 ($SiNH_2$) was found to arise from one of the fragments of these $Si_xN_yH_z$ species (AMU 77).[4,11] From QMA at 300°C and 500°C, the signal at AMU 47 ($SiNH_5$) was found to be independent of substrate temperature, while the signal at AMU 44 decreased at high substrate temperature.[11] This implies that there are few $Si_xN_yH_z$ species with high atomic mass, even at 500°C. Therefore, it is considered that $SiNH_5$ is dominant in the chamber at 500°C, compared with $Si_xN_yH_z$ species with higher atomic mass.

3.2 *Hysteresis*

Figure 6 shows 1 MHz C–V characteristics, with hysteresis, of Al/thick SiN_x/thin SiN_x/n c-Si diodes, where thin SiN_x layers were deposited with F_{NH3}/F_{SiH4} of (a) 120 and (b) 0.5. The broken curve represents data for a bias change from −10 V to 10 V, and the dotted curve exhibits data for bias from 10 V to −10 V. Here, the solid curve represents a theoretically calculated curve. Based on the direction of hysteresis, this hysteresis arises from charge injection due to tunneling from c-Si into SiN_x. In this study, the largest ΔV_h was 10 V, while the smallest was 0.10 V.

In the condition of accumulation or inversion, the injection or ejection of charged carriers for hysteresis occurs due to tunneling between the interface and deep levels in SiN_x. The injected carriers are trapped at such deep levels and they cannot be emitted into the extended states of SiN_x during the duration of measurement. Since the current transport mechanism under low electric fields ($\leq$ 1.4 MV/cm) in SiN_x is ohmic conduction, the injected carriers cannot move into the electrode (Al). This indicates that the injected carriers are considered to be stored near the interface in SiN_x. Therefore, an apparent

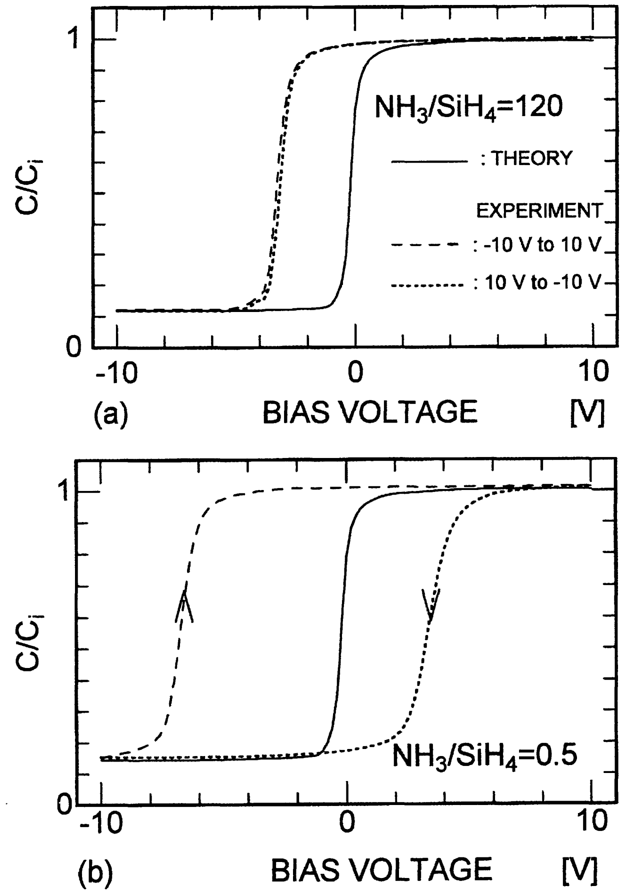

Fig. 6. 1 MHz C–V characteristics of Al/thick SiN_x/thin SiN_x/n c-Si diodes with thin SiN_x deposited with F_{NH3}/F_{SiH4} of (a) 120 and (b) 0.5.

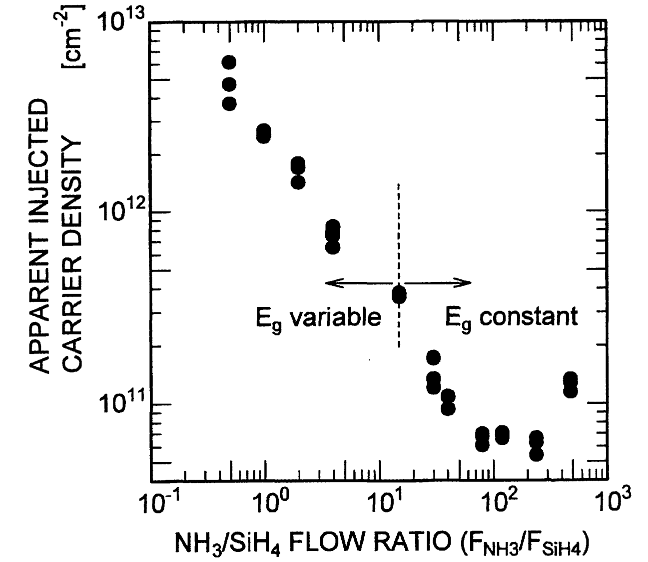

Fig. 7. Dependence of apparent injected carrier density on NH_3/SiH_4 flow ratio for thin SiN_x.

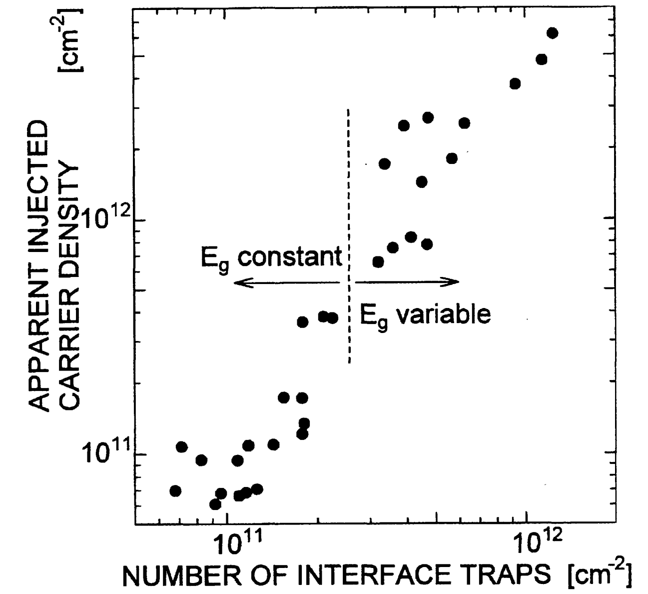

Fig. 8. Relationship between apparent injected carrier density and number of interface traps.

injected carrier density (N_{ic}) can be defined as $C_i \Delta V_h / q$, similarly to the definition of the fixed charge density for flatband voltage shift.[12] In this expression, C_i is the capacitance of the insulator and q is the charge of an electron.

Figure 7 depicts the relationship between N_{ic} and F_{NH3}/F_{SiH4}. Here, ΔV_h of 1 V approximately corresponds to N_{ic} of 5×10^{11} cm^{-2} in this study. The value of N_{ic} decreased with increasing F_{NH3}/F_{SiH4} below 80, and became constant. It then increased when $F_{NH3}/F_{SiH4} = 480$.

The band gap (E_g) of SiN_x is reported to increase from 3.2 eV to 5.3 eV with an increase in the N/Si atomic ratio from 1.00 to 1.33 in the theoretical calculation.[13] Therefore, E_g increases with increasing F_{NH3}/F_{SiH4} from 0.5 to 15, based on Fig. 5, and then E_g is saturated at 5.3 eV, as is clear in the figure. The change in the barrier height for tunneling from the interface into SiN_x follows the change in E_g. It is reasonable that N_{ic} decreases with increasing F_{NH3}/F_{SiH4} below 15 because of an increase in the barrier height.

Carrier injection should vary not only with the barrier height but also with the density of initial states for tunneling. If the initial states for tunneling are the extended states (i.e., the conduction band or the valence band), the density of the initial states is constant. Therefore, N_{ic} should be constant in $15 \leq F_{NH3}/F_{SiH4} \leq 240$ because of the constant barrier height. However, N_{ic} decreased with F_{NH3}/F_{SiH4}.

Interface traps are one of the candidates for the initial states. Figure 8 shows the relationship between N_{ic} and the number of interface traps (i.e., the integrated value of D_{it} over the energy range shown in Fig. 4). Since N_{ic} changed with the number of interface traps, carrier injection probably occurred from the interface traps. In particular, this is true for the case of samples prepared with $F_{NH3}/F_{SiH4} \geq 15$ because of constant E_g. In all samples, from the discussion above, N_{ic} is considered to depend not only on the barrier height for tunneling but also on the number of interface traps.

3.3 *Fixed charges*

A fixed charge density (N_{fc}), which arises from charged

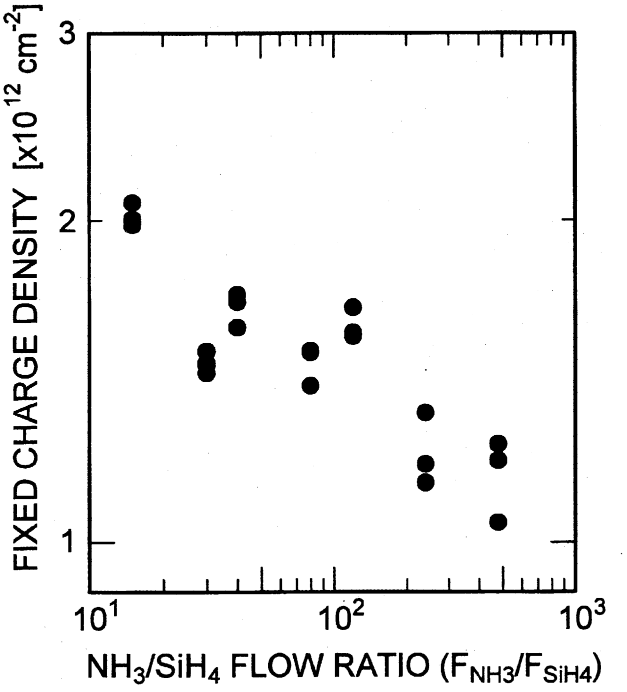

Fig. 9. Relationship between fixed charge density and NH_3/SiH_4 flow ratio for thin SiN_x.

states located near the interface in SiN_x, must ideally be zero, or realistically around 10^{10} cm^{-2}, where N_{fc} is given by $C_i \Delta V_{FB}/q$.[12] Figure 9 shows the relationship between N_{fc} and F_{NH3}/F_{SiH4}. Although N_{fc} could decrease with increasing F_{NH3}/F_{SiH4}, the values were much larger than the desirable value of 10^{10} cm^{-2}. Reduction of N_{fc} is now in progress.

4. Conclusion

We aimed to fabricate good-quality Al/SiN_x/c-Si MIS diodes by direct photo-CVD in a NH_3/SiH_4 gas system using a HF-treated c-Si substrate. In order to improve the interface electronic properties, a thin SiN_x layer was deposited with various F_{NH3}/F_{SiH4} before a thick SiN_x layer was deposited with $F_{NH3}/F_{SiH4} = 30$. By using the NH_3/SiH_4 flow ratio of 120, minimum interface-trap density (around 3×10^{10} cm$^{-2}\cdot$eV^{-1}) and hysteresis (about 0.1 V) of Al/thick SiN_x/thin SiN_x/c-Si diodes were obtained. By changing F_{NH3}/F_{SiH4} in the deposition of thin SiN_x, it was found that SiN_x should be deposited on c-Si only from $Si_xN_yH_z$ species (probably $SiNH_5$). The hysteresis of the C–V characteristics was found to arise from carrier injection through interface traps, and was found to depend on the number of interface traps and the N/Si atomic ratio in thin SiN_x.

Acknowledgements

This work was partially supported by a Grant-in-Aid on Priority-Area Research on "Photo-Excited Process" from the Ministry of Education, Science, Sports and Culture. This research was carried out at the Kyoto University Venture Business Laboratory.

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