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Fast Direct Nitridation of Silicon with Nitrogen Plasma and Its Effect on the Shift of Flat-Band Potential

Nobuteru Takeda, Hikaru Kobayashi,* and Hiroshi Tsubomura*

Laboratory for Chemical Conversion of Solar Energy and Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

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Silicon nitride films are produced by the reaction of crystalline silicon with nitrogen plasma, and the nitride films are studied by means of Auger electron spectroscopy, X-ray photoelectron spectroscopy, and work function measurements. The growth rate of the nitride film is very high at the initial stage; a 2-nm-thick Si nitride film is formed in 20 s by the reaction at 700 °C. The work function of the Si (100) surface increases slightly at the very initial nitridation stage and decreases by further nitridation. The work function of the (111) surface, on the other hand, decreases from the initial nitridation stage. The work function decrease is attributed to the nitrogen atoms below the surface. The change in the work function of the Si (100) surface is much larger than that for the Si (111) surface, because the (100) surface has an open structure. The Si electrode coated with a 2-nm-thick nitride layer shows a large anodic shift (maximum 1.5 V) in the flat-band potential after sweeping the electrode potential in an acetonitrile solution of $LiClO_4$. This shift is caused by Li^+ ions included in the oxynitride layer formed from the nitride film by the reaction with a small amount of water in the solution.

Introduction

The study of silicon nitride layer is important not only from a scientific point of view but also from the viewpoint of technological application to metal–insulator–semiconductor (MIS) solar cells[1-3] and large-scale integration (LSI).[4-6] A Si nitride film has advantages over a thermally grown Si oxide layer because of the following: (i) Due to its dense structure, impurity diffusion as well as oxidation of Si is prevented. (ii) Si nitride is less reactive with metals and is stable upon radiation. Therefore, MIS or photoelectrochemical (PEC) cells with Si nitride layers are expected to be more stable than those with oxide layers.

Direct nitridation of Si is carried out usually by heating Si in nitrogen[7] or ammonia atmosphere.[8-10] Heating at high temperatures is required for nitridation with nitrogen gas, which decreases the minority carrier diffusion length and enhances diffusion of dopants. Si reacts with ammonia gas at a relatively low temperature (700 °C).[9] The reaction rate is increased by deposition of a small amount of alkali metal,[11] by UV light illumination,[12,13] or by electron beam irradiation.[14] The nitridation temperature can also be lowered by the reaction with atomic nitrogen.[15-17] Nevertheless, the rates of the formation of the nitride films by these procedures are low and may be unsuitable to large-scale production. Si nitride films can also be grown by the reaction with ammonia plasma[18,19] or nitrogen–hydrogen plasma.[20] In these cases, however, plasma damage may be introduced, possibly by the incidence of high-energy ions or electrons. In the present study, Si nitride films are formed with a high rate by the reaction of Si with nitrogen plasma at a relatively low temperature (700 °C). During the film formation, the plasma damage is minimized by applying appropriate potential to the Si samples.

Formation of a high energy barrier is desirable for obtaining high photovoltages from solar cells. For this purpose, artificial control of the flat-band potential (hereafter abbreviated E_{FB}) may be required. In past MIS studies, this was achieved by forming thick insulating layers[21-23] or by confining ions in oxide layers by evaporation.[24] We have recently developed an electrochemical procedure to cause a large shift in E_{FB} by the inclusion of ions in thin Si oxide layers.[25] In the present work, this technique is applied to the thin Si nitride layers, and a shift much larger than that for the Si oxide layers is achieved.

Experimental Section

The semiconductor electrodes were prepared from n-Si (111) (phosphorus-doped, 2.4–4.0 Ω cm), p-Si (111) (boron-doped, 1.3–3.0 Ω cm), n-Si (100) (phosphorus-doped, 0.7–1.3 Ω cm), or p-Si (100) (boron-doped, 0.4–0.6 Ω cm) wafers. The Si wafers were etched with 10% hydrofluoric acid (HF) and washed with deionized water. The Si specimens were then mounted in an ultrahigh-vacuum (UHV) chamber (base pressure $\sim 2 \times 10^{-10}$ Torr) in which an Auger electron spectrometer (AES), a Kelvin probe, and an ion gun were installed. Clean Si surfaces were carefully produced by repeating Ne^+-ion bombardment (500 V, 5–7 $\mu A\ cm^{-2}$) and annealing at 700 °C. No impurities were observed on the Si

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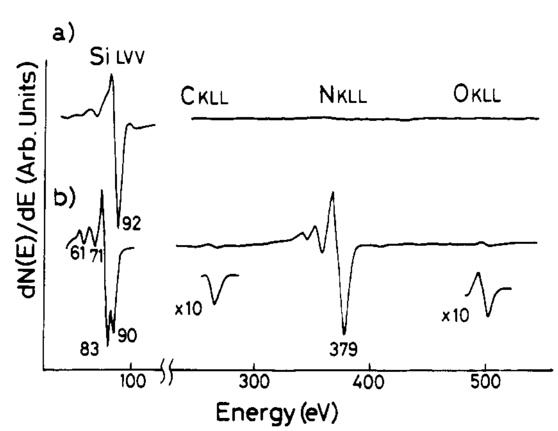

Figure 1. AES spectra in the derivative ($dN(E)/dE$) mode measured at 20 °C: (a) for the Si (100) clean surface; (b) for the Si (100) surface after 5 s of nitridation at 700 °C with nitrogen plasma.

surfaces thus prepared within the detection limit of AES. The Si specimens were heated by direct Joule heating, and the temperature was monitored with an optical pyrometer.

Nitridation was carried out by exposing the Si samples heated at 700 °C to nitrogen plasma, which was produced by applying 23 V between a tungsten filament at 1300 °C and a grid in a 10^{-2}-Torr nitrogen atmosphere. The emission current from the filament during nitridation was 0.12 A unless otherwise noted. An appropriate potential was applied between the grid and the Si sample so that no current was detected at the sample position, for minimizing the plasma damage.

In situ AES measurements were made by means of cylindrical Auger optics (PHI Model 06-150) at an electron beam energy of 3 keV in the normal incidence mode. The ac modulation voltage was 2 V. Work function changes ($\Delta\phi$) were measured with a Kelvin probe in which a 2 × 3 mm^2 gold plate was vibrated by a 2 × 6 mm^2 piezoceramic foil, supplied from Kyoto Ceramic Ltd., similar to that reported in ref 26. The amplitude and the frequency of the ac potential applied to the piezoceramic foil were 1.5 V and 150 Hz, respectively. The gold reference electrode was exposed to nitrogen plasma for several hours before the measurements in order for the electrode work function to be unchanged by subsequent exposure.

XPS measurements were carried out with a Shimadzu ESCA 750 spectrometer. Photoelectrons were excited by Mg Kα radiation. The Ag $3d_{5/2}$ peak was used as an energy standard (368.2 eV) in the experiment to determine the band bending, and in other cases the contaminant carbon 1s peak was used as the reference (285 eV). The base pressure in the XPS chamber was ~1 × 10^{-9} Torr. Si nitride films were produced also in the XPS chamber by the same procedure as that mentioned above.

Nitridation of the HF-etched Si without ion bombardment and annealing was performed at room temperature by the reaction with nitrogen plasma in a relatively low vacuum chamber (base pressure 10^{-6} Torr).

After the Si nitride films were formed, the Si samples were taken out of the vacuum chambers to make electrodes. Ohmic contact was made with an indium–gallium alloy at the rear Si surface, and then the sample was encapsulated with epoxy resin. The electrode thus prepared was immersed in a 1 M acetonitrile solution of $LiClO_4$ containing a small amount of molecular sieve. The electrode potential was swept in the solution at the rate of 8 mV s^{-1} with a potentiostat and a potential sweeper. A platinum plate and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The SCE was kept in a separate cell containing a solution with a composition identical with that of the main cell. A liquid junction was used to connect both the cells. The shift in E_{FB} was determined from the Mott–Schottky plots measured with an impedance analyzer (Hewlett-Packard, Model 4192A) at an ac frequency of 1 kHz and an amplitude of 5 mV.

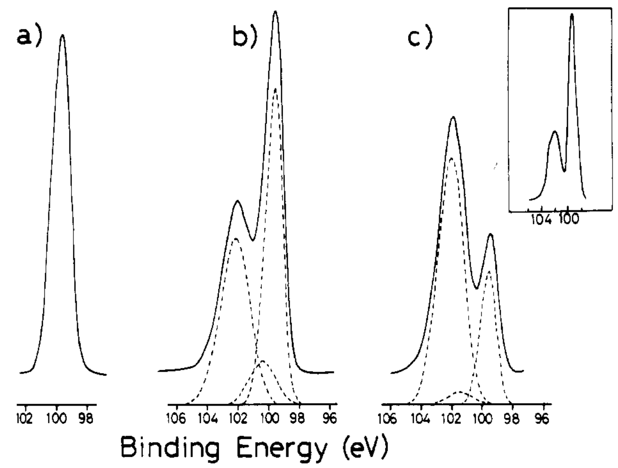

Figure 2. XPS spectra measured at 20 °C: (a) for the Si (100) clean surface; (b) for the Si (100) surface after 20 s of nitridation at 700 °C with nitrogen plasma; (c) for the Si (100) surface after 1 h of nitridation at 700 °C. The inset shows the XPS spectrum for the HF-etched and uncleaned Si (100) surface after 30 s of nitridation at room temperature with nitrogen plasma.

Results

Figure 1 shows the AES spectra for the Si (100) surface before and after the nitrogen plasma treatment. Before the treatment, the Si LVV peak was observed at 92 eV, and no peaks due to impurities were detected. After nitridation at 700 °C for 5 s, the Si LVV peak shifted to 90 eV, and new peaks due to Si nitride appeared at 83, 71, and 61 eV. The intensity of the peak at 83 eV was higher than that of the 90-eV peak. A strong N KLL peak was observed at 379 eV, and small peaks appeared in the C KLL and O KLL regions. The intensities of the nitride-induced Si LVV and N KLL peaks increased with the nitridation time, but the energy positions were unchanged. The 90-eV peak disappeared almost completely after nitridation for 20 s. The intensities of the N KLL peaks observed after nitridation of the (100) and (111) surfaces for the same periods were almost identical.

Figure 2 shows the XPS spectra for the Si (100) surface before and after nitridation at 700 °C. The 99.5 eV Si 2p peak observed for the clean surface showed no shift after nitridation, and a new peak appeared at 101.9 eV with the full width at half-maximum (fwhm) of 2.2 eV, 1.0 eV wider than the 99.5-eV peak. The intensity of the 101.9-eV peak increased with the nitridation time, but the peak position was unchanged. The structure in the Si 2p region can be resolved into three peaks as shown by the broken lines. The intensity of the peak in the middle position for 20-s nitridation was 22% of that of the 101.9-eV peak and decreased to 5% after 1 h of nitridation. The inset shows the XPS spectrum observed when the HF-etched and uncleaned Si surface was exposed to nitrogen plasma for 30 s at room temperature. In this case, a shifted Si 2p peak was present at 102.3 eV with a shoulder in the higher energy side.

Figure 3 plots the thickness of the Si nitride film formed at 700 °C as a function of the nitridation time. Assuming that the electron mean free path, λ, and the photoionization (or Auger) cross section in the Si nitride film are the same as those in the Si substrate and that photoelectrons (or Auger electrons) decay exponentially with the distance from the surface, the thickness of the nitride layer, d, is obtained from the following equation:

$$\frac{I_{SiN}}{I_{Si}} = \frac{D_{SiN}}{D_{Si}}[\exp(d/\lambda) - 1]$$

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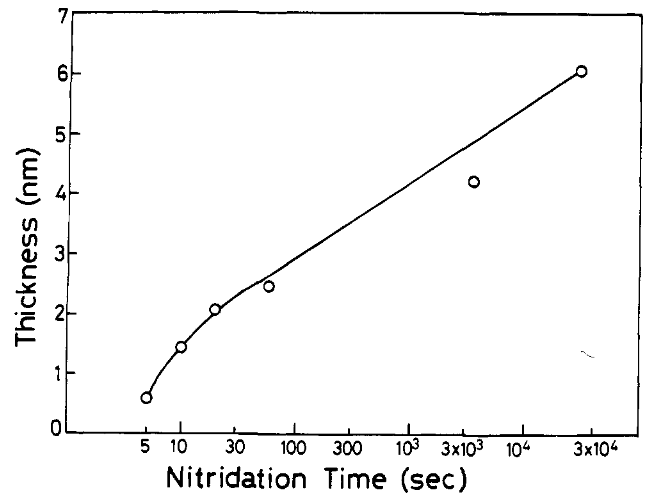

Figure 3. Thickness of the Si nitride film as a function of the time for the nitridation of the Si specimen heated at 700 °C with nitrogen plasma. The thickness for the nitridation time less than 10 s is determined from the AES results, while the XPS spectra are used to estimate the thickness for the time more than 20 s.

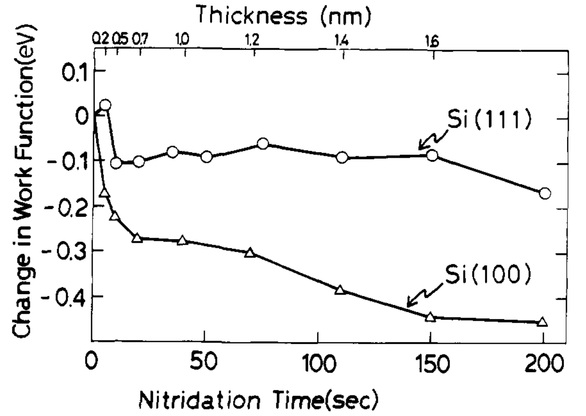

Figure 4. Work function changes of the Si (100) and (111) surfaces as a function of the nitridation time. The thickness of the nitride film is shown in the upper portion of the figure.

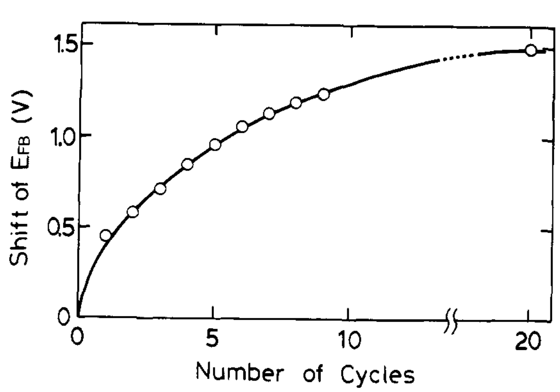

Figure 5. Amount of the shift in E_{FB} for the Si (100) electrode covered with the 2-nm-thick nitride layer as a function of the number of the potential sweep cycles between −1.0 and 1.0 V vs SCE. The nitride films are produced by exposing the Si samples heated at 700 °C to nitrogen plasma for 20 s.

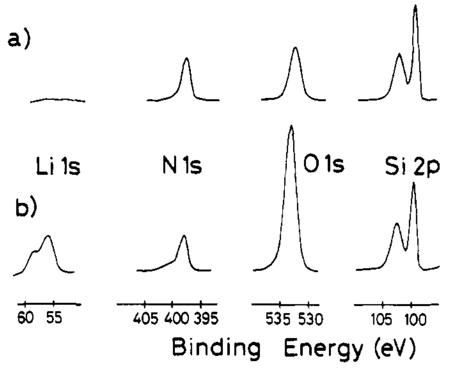

Figure 6. XPS spectra for the 2-nm-thick nitride-coated Si (100) electrodes: (a) after immersing in a 1 M acetonitrile solution of $LiClO_4$ for 30 min without applying potential; (b) after 20 cycles of the potential sweep between −1.0 and 1.0 V vs SCE in the same solution.

where I_{SiN} and I_{Si} are the intensities of the Si 2p (or LVV) peaks for the nitride and for the Si substrate, respectively, and D_{SiN} and D_{Si} are the densities of the Si atoms in the Si nitride film and in the Si substrate, respectively. In the calculation, D_{Si}/D_{SiN} was taken as 1.22, assuming that D_{SiN} for the Si nitride film is the same as that for the crystalline Si nitride.[27] The film thickness for the nitridation time less than 10 s was estimated from the AES results with λ of 0.45 nm,[28,29] and that for more than 20 s was obtained from the XPS results with λ of 3 nm.[30] The rate of the formation of the Si nitride film was very high (about 0.1 nm s^{-1}) in the initial nitridation stage up to the 2-nm thickness and then became slower. The film thickness after 8 h of nitridation was 6 nm.

Figure 4 shows the work function change, $\Delta\phi$, of the Si (111) and (100) surfaces as a function of the nitridation time. The thickness of the nitride film determined from the AES spectra is also shown in the upper portion of the figure. Only the data for the n-Si surfaces are presented, since p-Si showed almost the same $\Delta\phi$. For the purpose to measure $\Delta\phi$ caused during the initial nitridation stage in detail, the reaction rate was suppressed by lowering the temperature of the filament, and accordingly the emission current decreased from 0.12 to 0.01 A. The work function of the Si (111) surface increased after the formation of the 0.2 nm-thick nitride film and decreased by further nitridation. The work function of the Si (100) surface, on the other hand, decreased monotonically with the nitridation time. The $\Delta\phi$'s of the Si (100) and (111) surfaces after 200 s of nitridation were −0.17 and −0.45 V, respectively.

Figure 5 shows the shift in E_{FB} for the n-Si electrode covered with the 2-nm-thick nitride layer as a function of the number of the potential sweep cycles between −1.0 and 1.0 V vs SCE. E_{FB}'s for the n- and p-Si electrodes shifted toward the anodic potential with the cycles. The amount of the shift for the p-Si electrode was smaller by 30% than that for the n-Si electrode, similar to the case for the Si oxide layers.[25] Most of the shift occurred during the initial 10 cycles, and the E_{FB} value was stabilized after 20 cycles. The shift reached about 1.5 V after 20 cycles. In cases where the Si nitride film contained 15% oxygen in atomic concentration, the shift became about half.

Figure 6 shows the XPS spectra for the Si electrode with the 2-nm-thick nitride overlayer. Spectrum a was recorded after immersing the electrode in a 1 M acetonitrile solution of $LiClO_4$ for 30 min without applying bias, and spectrum b was for the same electrode after 20 cycles of the potential sweep between −1.0 and 1.0 V vs SCE in the same solution. After the potential sweep, the Si 2p peak initially observed at 101.9 eV was shifted to 103.0 eV and broadened. In the Li 1s region, no peak was present in spectrum a, and a peak

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and a shoulder were observed at 55.8 and 57.8 eV, respectively, in spectrum b. This result indicates that Li is included in the layer by the mechanism other than simple diffusion. The O 1s peak was increased in intensity after the potential sweep.

Discussion

In the present study, nitridation of Si in the early stage is studied extensively, since insulating layers of thickness below 2 nm are required for MIS solar cells. In the present study, effort was made to form pure Si nitride layers, in order to investigate the nature of the nitride film and to cause a large E_{FB} as shown later.

Thermal reaction of Si with nitrogen gas proceeds only at temperatures above 1200 °C.[7] Thermal nitridation of Si with ammonia gas occurs at lower temperatures, but the reaction rate is very low. The thickness of the films formed in 7 h by the reaction with 1 atm of ammonia at 900, 1000, and 1100 °C is 4.0, 4.7, and 6.0 nm, respectively.[9] On the other hand, the present study has shown that the reaction of Si with nitrogen plasma proceeds much faster. The reaction rate at 700 °C in the initial nitridation stage up to the 2-nm-thick nitride formation is about 0.1 nm s^{-1}, about 3 orders of magnitude higher than that for the direct nitridation with ammonia gas at 1000 °C. The concentrations of O and C atoms are estimated both about 1/30 of that of N atoms on the basis of Figure 1b, indicating that contamination can be eliminated by the fast reaction. It is noted that oxygen is easily incorporated in nitride films since Si oxide is thermodynamically more stable than Si nitride, and hence in most of the works on the direct nitridation of Si,[4,7,8,10] Si oxynitride films were produced instead of Si nitride. The tungsten filament used in this work is very stable in the nitrogen atmosphere without reaction or evaporation. Therefore, no tungsten is present in the nitride layer.

It is shown in the inset in Figure 2 that the Si specimens that are HF etched but not cleaned by ion bombardment and annealing can be nitrided. In this case, Si oxynitride is produced because of the presence of the thin Si oxide layer at the surface and of the incorporation of water and oxygen in nitrogen plasma due to the relatively low vacuum (base pressure 10^{-6} Torr). Therefore, this procedure seems to be applicable to the mass production of thin insulating layers in MIS solar cells because of the high reaction rate and of the simple apparatus with a relatively low vacuum chamber and a simple ionization device for producing plasma.

Direct comparison of the initial nitridation rate for the present study with those reported previously[19,20] using RF plasma seems difficult to make since relatively thick nitride films were formed. Ito et al.[18] formed a ~5-nm-thick Si oxynitride layer for 20 min by the reaction of uncleaned Si heated at 1050 °C with RF-activated ammonia plasma. Hezel et al.[31] studied the early stage reaction of the uncleaned Si heated at 340 °C with NH_3/H_2 plasma and reported the formation of the oxynitride layer of about 2-nm thickness after 2 min of nitridation. The reaction rates for the present procedure and those observed in refs 18 and 30 may be almost identical if nitridation is performed at the same temperature with clean Si.

The shift of the substrate Si LVV peak from 92 (Figure 1a) to 90 eV after 5 s of nitridation (Figure 1b) is caused by the annihilation of the Si dangling bonds owing to the Si–N bond formation.[32] The spectral shape between two peaks at 90 and 83 eV shows no indication of the existence of intermediate nitride species, which were observed for nitridation at low temperature.[33] The 90-eV peak disappears completely after 20 s of nitridation, indicating that free Si atoms[34] are not present in the nitride layer. The energy positions of the nitride-induced peaks (83, 71, and 61 eV) are almost identical with those for stoichiometric Si nitride,[35] indicating that the electronic structure of the thin nitride layer is similar to that of stoichiometric nitride.

The nitride-induced Si 2p peak is observed at 101.9 eV (Figure 2b), 2.4 eV higher than the Si substrate peak. It is suggested that the Si atoms bound to four, three, two, and one nitrogen atoms shows Si 2p peaks shifted by 2.7, 1.5, 0.8, and 0.3 eV, respectively, from the Si substrate peak.[36] Thus, the 101.9-eV peak is attributed to Si bound to four N atoms. The experimental curve in the Si 2p region observed after 20 s of nitridation can be resolved into two peaks at 101.9 and 100.1 eV. The intensity of the 100.1-eV peak is 22% of that of the 101.9-eV peak. The 100.1-eV peak is attributed to the nonstoichiometric Si nitride species. If this species is present in the surface region or in the nitride bulk, the intensity of the 100.1-eV peak is expected to be hardly changed with the thickness of the nitride film. However, this peak is found to be reduced in intensity with the thickness as shown in Figure 2c, and thus the nonstoichiometric nitride is present most likely in the Si nitride/Si interfacial region.

The atomic ratio of Si and N for the 2-nm-thick Si nitride film is calculated to be 1:1.2 from the ratio of the integrated intensities of the 101.9-eV Si 2p peak and the N 1s peak. In this estimation, the 100.1-eV Si 2p peak is not included. A small deviation of the ratio from the stoichiometric Si nitride value of 1:1.33 is caused probably by the presence of the nonstoichiometric nitride species. For the thicker nitride films, this ratio becomes 1:1.30, closer to that of the stoichiometric value.

The fwhm of the nitride-induced Si 2p peak at 101.9 eV is 2.2 eV, 1.0 eV wider than the substrate Si 2p peak. This broadening is caused probably by the presence of the Si atoms with various N–Si–N bond angles[37] resulting in statistical fluctuations of charge distribution on the Si atoms. Another cause may be the electron–phonon coupling.[38]

Generally, $\Delta\phi$ of semiconductors is changed by either the change of the band bending or the dipole moment. The Kelvin method detects the sum of both factors, while the energy position of the substrate XPS peak depends only on the band bending. In the present case, the energy position of the Si 2p substrate peak with respect to the Ag $3d_{5/2}$ reference peak is not changed upon nitridation, and therefore it is concluded that observed $\Delta\phi$ is caused by the change of the dipole moment.

The dipole moment of the Si–N bond points from the N atom to the Si atom. Hence, an increase in the work function observed at the very initial stage of nitridation of the Si (111) surface indicates that most of the N atoms are present above the Si surface. The subsequent decrease in the work function is caused by the diffusion of the N atoms below the Si surface. The work function of the Si (100) surface, on the other hand, decreases monotonically

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with the nitridation time, showing that the N atoms enter the Si substrate even at the initial stage of nitridation. This difference in the initial $\Delta\phi$ might arise from the different geometrical structures of the surfaces. Namely, the (111) surface has the most closely packed structure while the (100) surface has an open structure, and therefore N atoms diffuse into the Si (100) substrate more easily than into the (111) substrate. Similar work function changes were observed in the oxidation of the Si (111) and (100) surfaces.[39]

For forming relatively thick nitride films, reorganization of the surface Si atoms must occur, and thus the structures of the nitride surfaces as well as the bulks formed on the Si (100) and (111) substrates are thought to be the same. On the other hand, the nitride/Si interfacial regions are likely to have different structures due to the difference in diffusion coefficient of N atoms in the (100) and (111) substrates, causing different $\Delta\phi$ after the formation of the relatively thick nitride layers. The Si 2p peak at 100.1 eV may be caused by the N atoms which diffuse into Si.

E_{FB} for the 2-nm-thick nitride-covered Si electrodes is shifted in the anodic direction after sweeping the electrode potential in the 1 M acetonitrile solution of $LiClO_4$ as shown in Figure 5. This indicates that the barrier height in Si can be controlled by this simple electrochemical method. A similar shift is observed for the Si electrodes covered with the thin Si oxide layers,[25] but the amount of the shift is about one-third of that for Si nitride.

After the potential sweep, the nitride-induced Si 2p peak shifts from 101.9 to 103.0 eV (Figure 6b), indicating that the Si atoms in the layer are more positively charged. Simultaneously, the intensity of the O 1s peak is increased. These results indicate that Si oxynitride is formed from Si nitride, probably by the reaction of the nitride film with a small amount of residual water in the acetonitrile solution.

After the potential sweep, a Li 1s main peak and a shoulder are observed at 55.8 and 57.8 eV, respectively. The 55.8-eV peak is assigned most probably to Li bound to other atoms, and the 57.8-eV peak to free Li^+ ions.[25] The shift in E_{FB} caused by the former species is thought to be very small since the dipole moments of the bonds are randomly oriented. On the other hand, free Li^+ ions in the layer will shift E_{FB} because they generate a potential drop in this layer. As the Si band edges are fixed with respect to the band edges of Si oxynitride, the Si band edges are shifted by the same amount as that of the potential drop in the oxynitride layer. If one assumes that Li^+ ions are present uniformly in the layer of the 2-nm thickness and the dielectric constant of the layer is 4, the density of Li^+ ions to cause a 1.5-V shift in E_{FB} is estimated to be 1.7×10^{20} cm^{-3}. The Li^+ ions are thought to be included in the film during the transformation from nitride to oxynitride. This is supported by the fact that the shift becomes smaller when the as-produced Si nitride layer contains a large amount of oxygen.

Our recent work[25] shows that Li^+ ions can be included in the Si oxide layer only during the formation of the layer in the solution, but cannot after the formation. Contrary to this case, inclusion of Li^+ ions in the nitride layer is possible after the film formation.

Conclusion

The rate of the Si nitride formation by the reaction of Si with nitrogen plasma at 700 °C is at least 2 orders of magnitude higher than that by the reaction with ammonia at 900 °C, and consequently contamination during the film formation can be minimized. This procedure may be applicable to the mass product of Si nitride (or Si oxynitride) films in MIS solar cells as well as in LSI. The work function of the Si (111) surface increases slightly in the very initial nitridation stage and decreases by further nitridation. The work function of the (100) surface decreases monotonically. The amount of the work function lowering of the (100) surface is more than twice of that of the (111) surface, due to the open surface structure. E_{FB} for the nitride-covered Si electrode is shifted toward the anodic (maximum 1.5 V) after the electrode potential sweep in the acetonitrile solution of $LiClO_4$. This shift is caused by the inclusion of the Li^+ ions in the Si oxynitride layer which is formed from Si nitride during the potential sweep. This electrochemical procedure can be applied to the MIS and PEC solar cells to enhance the energy barrier and the photovoltage.

Registry No. Si, 7440-21-3; N, 7727-37-9; Li, 7439-93-2; silicon nitride, 12033-89-5; silicon oxynitride, 12033-76-0.

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Oxygen Stoichiometry and Expansion of $YBa_2Cu_4O_8$

H. M. O'Bryan,* J. E. Graebner, W. W. Rhodes, S. Jin, and R. A. Fastnacht

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

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The effects of temperature and oxygen partial pressure on the oxygen stoichiometry, expansion, and electrical resistivity of $YBa_2Cu_4O_8$ have been determined. Samples prepared by two low-pressure synthesis methods—prolonged reaction between $YBa_2Cu_3O_7$ and $Cu(NO_3)_2$ and reaction between $BaCO_3$, Y_2O_3, and CuO at 4 Torr of oxygen—behave similarly. Heating to 800 °C in oxygen produces a loss of 0.08 atom of oxygen, which is completely recovered during cooling. At 500 °C a change of the ambient gas from pure oxygen to 0.25% oxygen causes a release of 0.055 atom of oxygen and an expansion of ~200 ppm. Two diamagnetic transitions, a weak one at 81 K and a strong one at 70 K, are observed. The average thermal expansion between 25 and 800 °C is 13.2 ppm/°C in oxygen.

Introduction

Early reports on the $YBa_2Cu_4O_8$ high-temperature superconductor (124) suggested that it possesses a relatively high T_c (~81 K) and an oxygen stoichiometry nearly independent of temperature. This latter behavior was expected to present a major advantage over $YBa_2Cu_3O_7$ (123) since oxygen replacement would not be required after high-temperature processing. In the course of preparing

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