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THIN FILM GROWTH AND SURFACE REACTION ON H-TERMINATED SILICON SURFACE

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ABSTRACT

We have investigated the effects of H atoms on thin film growth processes and surface reactions. In the oxidation of Si, Si surfaces are passivated against the O_2 adsorption by terminating dangling bonds with H atoms. Moreover, the existence of Si-H bonds on Si(100) surfaces enhances the structural relaxation of Si-O-Si bonds due to a charge transfer from Si-Si back bonds. In the heteroepitaxial growth of a Si/Ge/Si(100) system, H atoms suppress the segregation of Ge atoms into Si overlayers since the exchange of Ge atoms with Si atoms bound with H must be accompanied with breaking of Si-H bonds. However, 3-dimensional island growth is also promoted by atomic H irradiation, which is considered to result from the suppression of surface migration of adsorbed reaction species and from the lowering of step energies by the H termination of dangling bonds.

INTRODUCTION

Control of chemistry on Si surfaces is increasingly important for process technologies in ultra-large scale intergrated circuits(ULSI's) because the realization of well-efined surfaces and interfaces is essential for a reduction of device dimensions in ULSI. Recently, H-related reaction upon Si surfaces have been attracted attention for the control of surface reactions and H atoms adsorbed on surfaces have various effects on thin film growth processes. The chemical reactivity of Si surfaces becomes smaller by the termination of dangling bonds with H atoms, which can be applied to surface pass-ivation and selective growth. It has been found that the H-terminated Si surfaces are successfully obtained by a HF treatment[1, 2] and that the surfaces are passivated against native oxidation even in atmosphere[1, 3]. The H-termination treatment is promising as a new technology in controlling the formation of native oxide. The existence of H atoms on the surface lowers the surface energy or the interface energy between growth films and substrates. Hydrogen atoms on the growing surface also govern the surface migration of adsorbed reaction species on the surface. These effects can change the growth mode and the surface morphology, which are observed in heteroepitaxial systems such as Ge/Si[4, 5] and metal/Si[6] systems.

We have investigated the interaction between H atoms and thin film growth processes in the oxidation of Si and the

heteroepitaxial growth of Ge/Si. In this paper, the effects of H atoms on the growth processes are discussed. The main experimental data were obtained form high-resolution electron energy loss spectroscopy(HREELS), reflection high energy electron diffraction (RHEED)and scanning tunneling microscopy (STM).

RESULTS AND DISCUSSION

Initial oxidation of H-terminated Si(100) surfaces.

In this section, the influence of H atoms on the oxidation process of Si surfaces are presented. We discuss on the passivation of Si surfaces by H-termination and on the relationship between the relaxation of Si-O-Si structures and Si-H bonds on the surface.

Figure 1 shows the HREELS spectra of H-trminated Si(100)-1x1 surfaces(a) before and (b) after exposing to O_2 at room temperature[7]. The spectrum of a Si(100)-2x1 clean surface exposed to O_2 at room temperature is also shown in Fig. 1(c). The H-terminate surface was formed by exposing a Si clean aurface to H atoms at room temperature and H atoms were produced using a tungsten filament heated at 1500℃. Energy loss peaks of twisting (ν_{H1}), wagging(ν_{H2}), scissors(ν_{H3}) and stretching (ν_{H4}) modes for Si-2H species are observed in the spectrum of as-terminated Si(100) surfaces at 61, 78, 112 and 258 meV, respectively. Because the as-terminated surface, moreover, has a 1x1 structure, confirmed by lowenergy electron diffraction (LEED), a dihydride structure is formed on the H-terminated Si(100) surface. It is clearly found from Figs. 1(a)and 1 (b)that no adsorption of O atoms takes place on the H-terminated Si Surface. On the other hand, the dissoci ative adsorption of O_2 occurs on the clean surface evern at room temperature since there exist energy loss peaks of symmetric bending (ν_{O1}), symmetric stretching (ν_{O2}) and asymmetric stretching(ν_{O3}) modes for Si-O-Si species in the spectrum of Fig. 1 (c). These facts indicate that Si(100)surfaces are stable against the adsorption of O_2 by terminating dangling bonds with H atomes. We also found the the adsorption of O_2 H-terminated Si(100) surfaces does not start until the dangling bonds are revealed by the desorption of H atoms from the Si surface above

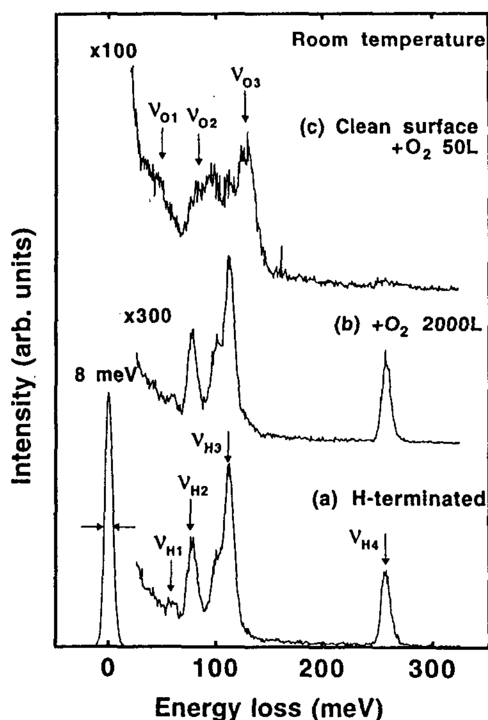

Fig. 1 HREELS spectra of H-terminated Si(100)-1x1 surfaces (a) before and (b) after exposing to O_2 at room temperature[7]. the spectrum of a Si(100)-2x1 clean surface exposed to O_2 at room temperature is also shown is this figure(c).

an oxidation temperature of 400℃[7]. This fact clearly supports the conclusion that the passivation of Si surfaces is realized by the H termination of dangling bonds.

In order to clarify the effect of Si-H bonds on oxidation processes and local bonding structures of SiO_2, oxidation of H-terminated Si surfaces was enhanced by thermal decomposition of O_2 with a tungsten filament heated at 1500℃. At oxidation temperatures below 300℃, a splitting of the loss peak of the Si-H stretching mode(ν_{H4})[8] and a shift in vibrational energies of the Si-O-Si asymmetric stretching mode (ν_{H2o3})were observed with progressing of oxidation[8,9]. These phenomena are closely related with the local bonding structrures.

The loss peak of the Si-2H stretching mode (ν_{H4}) split into two peaks with the loss energies of 258-269 and 277-280 meV, which include the information of Si-2H, O-Si-2H and O-Si-H(n=0,1 : n denotes the number of adjacent O atoms)Species, and of 2O-Si-2H, 2O-Si-H and 3O-Si-H(n=2, 3) ones, respectively[8,10]. Figure 2 shows the loss peak intensities of the Si-2H stretching mode for n=0,1 and n=2, 3 at 300℃ function of atomic O exposure[8]. the O coverage determined by Auger electron spectroscopy(AES), which is defined as the ratio of the number of adsorbed O atoms to that of (100) surface si atoms, are also indicated in Fig. 2. In this figure, the peak intensities are normalized to the total peak intensity. It is noticed that the intensity of the Si-2H stretching mode with two O atoms increases above 100L. At this exposure, the O coverage estimated by AES is about 0.8 ML. These results indicate that O atoms preferentially adsorb on one of a pair

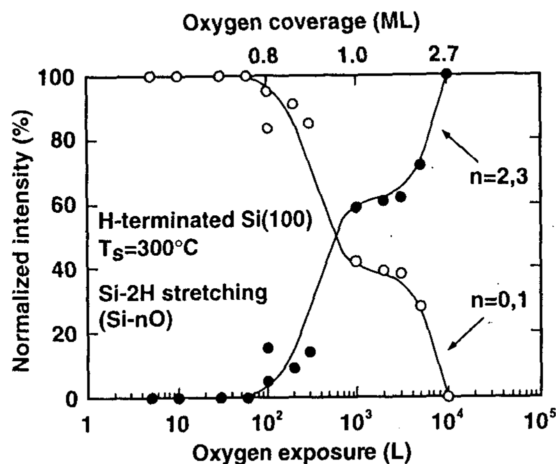

Fig. 2. Loss peak intensities of a Si-2H stretching mode for the si atom bonding with zero or on adjacent O atom=(n=0,1)and with two or three adjacent O atoms(n=2,3)at 300℃, function of atomic O exposure[8]. The O coverage determined by AES is also indicated in this figure. The peak intensities are normalized by the total peak intensity of the Si-2H and Si-H bonds.

of the Si back bonds until the O coverage is 0.8ML and then other adsorption sites. such as the other back-bond sites, start to be occupied by O atoms.

Figure 3 shows changes in the energy loss of the Si-O-Si asymmetric stretching mode(ν_{o3}) as a function of O coverage for clean and H-terminated Si(100) surfaces at room temperature and for H-terminated Si(100) surfaces at 300℃[8]. The experimental result for the thermal oxide grown at 850℃ is also shown in this figure. Two oxidation steps can be seen in the case of H-terminated surfaces: The energy of the loss peak remains constant for O coverages up to 0.8ML and then increases with increasing the O coverage. Finally, the energy saturates at about 1.8ML. The O coverages below 0.8ML corresponds with the oxidation step in which the O atoms pref

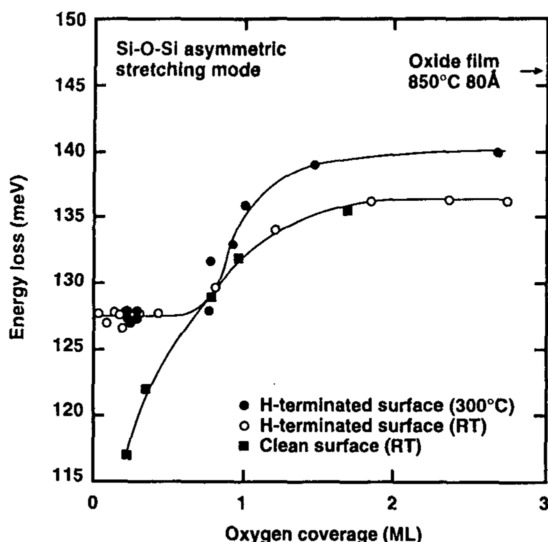

Fig. 3 Changes in the energy loss of a Si-O-Si asymmetric stretching mode as a function of O coverage for the oxidation of H-terminated Si(100) surfaces at room temperature and 300℃ and for clean Si(100) surfaces at room temperature[8]. Also shown in this figure is an experimental result for the thermal oxide at 850℃.

erentially adsorb on one of the two back-bond sites of a surface Si atom as mentioned above. The saturation value above 1.8ML only depends on the substrate temperature. The shift to higher vibrational energies suggests that the Si-O-Si bonds are relaxed above 0.8ML, since the Si-O-Si species of the thermally grown oxide at 850℃ have vibrational energy.

In the case of clean surfaces, a monotonous in crease in the energy loss with increasing the O exposure is observed in Fig. 3. Below 0.8ML, the energy loss of H-terminated surfaces is constant and is larger than that of clean surfaces, which suggests that the Si-O-Si bonds are relaxed by the existence of Si-H bonds. The bond strenght of Si-Si back bonds is considered to be weakened by a charge transfer from Si-Si back bonds to surface Si-H bonds because of the difference between electronegativities of Si and H. Therefore, the dflexibility in the formation of Si-O-Si structures increases and the structure can be relaxed. The increase in energy loss above 0.8ML means that the large structural relaxation in Si-O-Si bonds is induced when a surface Si atom has two Si-O bonds on H-terminated Si(100) surfaces. This structural relaxation in Si-O-Si is thought to be the cause of the preferential O adsorption as mentioned above.

Ge/Si heteroepitaxial growth

Next, we focus on the effects of H atoms on the interfacial abruptness and present the expermental results of Ge/Si heteroepitaxial growth. Figure 4 shows the growth rates of Si overlayers on Ge(2.5ML)/Si(100) using Si_2H_6-source molecular beam epitaxy(MBE) at 500℃ with and without atomic Hirradiat-

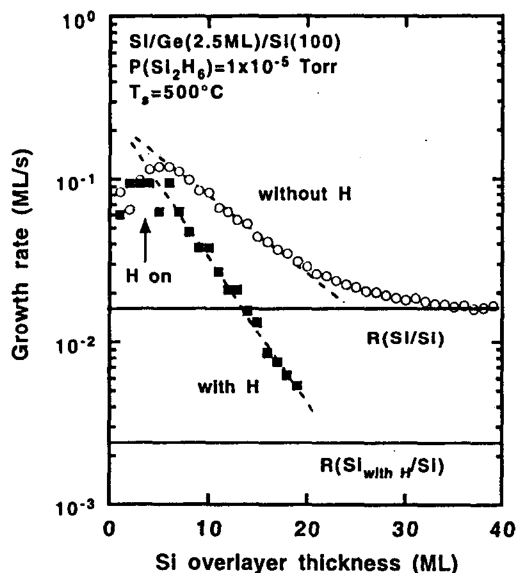

Fig. 4 Changes in the growth rate of Si overlayer on Ge(2.5ML)/Si(100)substrates with and without atomic H irradiation at a growth temperature of 500℃ and a Si_2H_6 gas pressure of 5×10^{-6} Torr, as a function of Si overlayer thickness[11]. The introduced H_2 gas pressure is 5×10^{-5} Torr.

ion, as a function of Si overlayer thickness[11]. The Ge(2.5ML)/Si(100) substrate was fabricated by growing Ge layers on Si(100) surfaces using GeH_4-source MBE at 475℃ after thermally cleaning the Si surface at 1, 200℃. The layer-by-layer growth rates and film thicknesses of Ge and Si were determined by RHEED intensity oscillation peiods of the specular spot. Two solid lines in this figure indicate the growth rates of the Si/Si (100) homoepitaxial growth with and without atomic H irradiation.

The growth rate os Si overlayers on Ge/Si (100) decreases exponentially with increasing the Si overlayer thickness, which corresponds to the change in Ge composition on the growing surface[12,13]. It has been reported that H atoms are desorbed at 425℃ on Ge surfaces[14] and that the desorpiton of H atoms from Si surfaces occurs at 500~600℃ [15]. Therefore, Ge atoms on the growing surface mainly acts as the dissociative adsorption of Si_2H_6 molecles since the growth rate is limited by the dissociative adsorption of Si_2H_6 on dangling bonds.

The growth rate, R, is given by the following equation[11,12]

$$R=(1-\theta_{ge})\cdot R_{Si/Si}+\theta_{ge}\cdot R_{Si/Ge,} \quad (1)$$

where $R_{Si/Si}$ and $R_{Si/Ge}$ are the growth rates of Si on Si and Ge surface atoms, respectively. θ_{Ge} is the surface coverage of Ge atoms on the growing surface and can be expressed as

$$\theta_{Ge}\propto \exp(-t/\lambda) \quad (2)$$

where is the Si overlayer thickness and λ the decay length of Ge surface coverage which characterizes the abruptness of Si/Ge interfaces.

The decay length for various Si_2H_6 pressures and substrate temperatures is summarized in Table 1[11,12]. the left and right values in each growth condition corresponds to the deday lengths for the Si growth without and with h, respectively. The mark-means that the growth mode of the Si overlayers is an island growth mode. It is noted that the influence of excess H atoms on the decay length and the growth mode differs with the growth conditions. The results in Table 1 can be divided into three classes:(1)the decay length hardly changes, (2) the decay length decreases remarkably and (3) the growth mode changes into an island growth mode. It is found from Table 1 that H atoms adsorbed on the growing surface play an important role in suppressing the segregation of Ge atoms.

Hydrogen atoms adsorbed on surface Si atoms are considered to mainly contribute to the suppression of Ge atoms since most of the H atoms are desorbed from Ge atoms as mentioned above. The relationship between the decay lengh of Ge atoms since most of the H atoms are desorbed from Ge atoms as mentioned above. The relationship between the decay length of Ge atoms in the Si overlayer growth on Ge/Si(100)and H coverage on Si atoms under the various growth conditions is shown in Fig. 5[16]. the H coverage wa estimated from the changes in growth rates of Si /Si(100) homoepitaxial growth using Si_2H_6-source MBE [16-18]. The decay lengths reported by solid-source MBE(SSMBE)[19] are also plotted in Fig. 5 as a case of $o_H=0$. A linear correlation between the decay length of segregated Ge atoms and the H coverage on Si atoms is obtained, regardless of the wide var-

Table 1 Decay lengths of Ge atoms in Si overlayers grown on Ge(2.5ML)/Si(100)at various Si_2H_6 Pressures and substrate temperatures[11,12]. The mark(-) means that the growh mode of the Si layers is an island growth mode. The marks(1), (2) and (3) indicate classes of the influence of excess H irradiation on the growth of Si overlayers, detailed in the text.

Decay length(ML)

Substrate temperature (℃)	Pressure of Si_2H_6(Torr)				
	1.2×10^{-6}	5.0×10^{-6}	1.0×10^{-6}	5.0×10^{-5}	1.0×10^{-4}
440	(2) 5.5 → 1.8	(2) 3.3 → 1.4	(1) 1.8 → 1.3	(1) 0.9 → 1.3	(1) 1.1 → 1.0
475	(3) 7.1 → –	(2) 5.0 → 3.7	(1) 2.6 → 2.4	(1) 1.8 → 1.9	(1)) 2.0 → 2.1
500	(3) 14.4 → –	(3) 9.2 → –	(2) 7.0 → 3.9	(1)) 4.2 → 4.3	(1) 3.3 → 3.1
550	(3) 33.1 → –	(3) 29.0 → –	(2) 16.0 → –	(1) 13.0 → 12.3	9.7 →

– : Island growth (Without H→ whit H)

iety of growth conditions. Furthermore, it should be noted that the decay length extrapolated to $O_H=0$ is very close to that obtained by SSMBE. These facts indicate that the decay length is predominantly determined by the H coverage on the surface Si atoms. The presence of Si-H bonds on the growing surface would hinder the exchange of surface Si atoms with Ge atoms at the subsurface, since an additional energy to break Si-H bonds is necessary for the exchange.

It should be noted in Table 1 that additional H atoms not only suppress the segregation of Ge atoms but also promote the 3-dimensional(3D) island growth of the Si overlayer. Next, the influence of H atoms on the surface morphology in Ge/Si(100) epitaxial growth are discussed. Figure 6 shows the STM images of 3-ML-Ge films grown on Si(100) surfaces using SSMBE at 500℃ (a) without and (b) with atomic H irradiation[5]. It is found from Fig. 3 (a) that the Ge film grows in the 2D island growth mode under

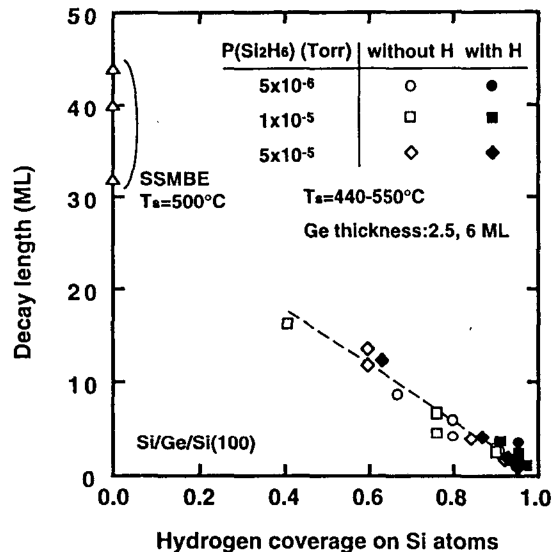

Fig. 5 Decay length of Ge atoms on Si over-layers on Ge/Si(100) substrates vs. H coverage on surface Si atoms under various growth conditions[16]. Decay lengths obtained by SSMBE[19] are also shown.

the growth condition without the additional H. The 2D islands have rectangular shapes and dark lines on the terraces are observed. The dark lines are due the ordering of miss-

ing dimer defects. The formation of the anisotropic shape of 2D islands is caused by the difference between the Ge sticking coefficients at the end and side of dimer rows. On the (100) surface, the edge of Ge 2D islands is locally oriented parallel or perpendicular to the dimer rows, which is called $S_A$or S_B steop, respectively [20]. Since the step energy of S_B is large than tat of S_A[20], Ge atoms can easily stick to the end of dimer rows.

By the addition of H atoms, on the other hand, the surface morphologies are varied dramatically, as shown in Fig. 3(b). The density of growth nuclei increases remarkably and the surface roughness is enhanced. The multilayered structure is observed, which is characterized by the stacking of parched-shape 2D islands, although the growth is still a 2D island growth mode. Therefore, the multiple nucleation and layer grwoth modes are promoted by the atomic H irradiation.

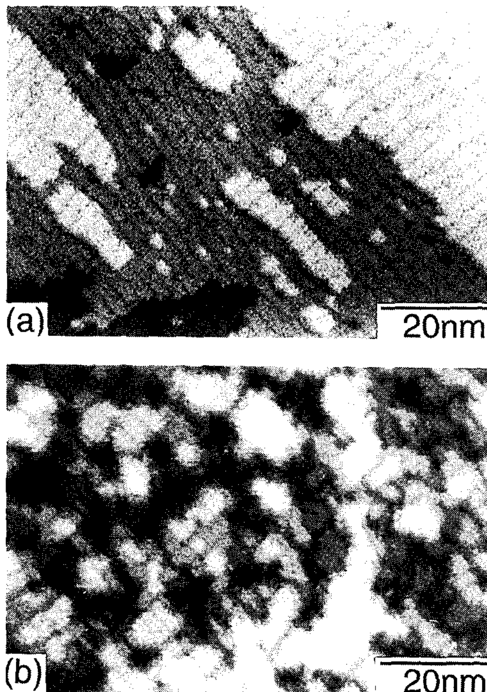

Fig. 6. STM images of Ge films on Si(100) surfaces grown at 500℃ (a) with and (b) without additional H atoms of $1.4 \times 10^{14} cm^{-2} s^{-1}$[5]. the Ge coverage is 3.0ML. The scan area is 171.0x114.5nm^2.

It is considered that these phenomena can be explained by both the kinetic and eneretic effects of the additional H atoms. The kinetic effect of the additional H atoms is due to a reduction of the diffusion length of Ge adatoms, which causes an incerase in the density of 2D nuclei and promotes the multiple nucleation and layer growth. As a result, the surface roughness is incerased with the progress of growth. On the other hand, the H adsorption on the step sites reduces the step energy by terminating dangling bonds. The step energy of S_B is considered to be lowered by H adsorption and to be close to that of S_A under condition with the additional H. Therefore, the shape of 2D islands becomes an isotropic shape, as seen in Fig. 3 (b).

Furthermore, since the H desorption from Ge monohydried occurs at lower temperature than that from Si monohydride, the H coverage on Ge terraces is considered to be lower than that on Si substrates at 500℃[14,15]. Hence, the growth nuclei can be more preferentially formed on the 2D Ge islang, which leads to an increase in the surface roughness.

CONCLUSIONS

We have investigated the effects of H atoms on growth processes and surface reactions and found various roles of H in the oxidation and heteroepitaxial growth.

Si surfaces are passivated by terminating dangling bonds with H atoms. Therefore, the oxidation by O_2 does not occur, until H atoms adsorbed on surface Si atoms desorb and

dangling bonds appear on the surface. In addition, the presence of Si-H bonds on Si (100) surfaces promotes the structural relaxation of Si-O-Si bonds formed on the surface. It is considered that the bond strength of Si-Si back bonds is weakened by Si-H bonds due to the difference between electronegativities of Si and H, which leads to an increase in flexibility of the formation of Si-O-Si bonds.

In the heteroepitaxial growth of a Si/Ge/Si (100) system, the segregation of Ge atoms into Si overlayers is suppressed by the existence of Si-H bonds on the growing surface, since and additional energy to break Si-H bonds is necessary for the exchange of surface Si atoms with Ge atoms at the subsurface.

Therefore, the decay length of Ge coverage is dominated by the H coverage on ehe surface Si atoms. However, excess H irradiation also promotes 3D island growth under a growth condition. The suppression of surface migration and the lowering of step energies by the existence of Si-H bonds are considered to enhance the island growth.

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