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Ge Epitaxial Overlayers on Si(001) Studied by Surface-Sensitive XAFS; Evidence for Strain-induced Surface Site Exchange

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The structure of Ge epitaxial overlayers on Si(001) (Ge_n/Si(001), n<6) has been studied by *in-situ* surface-sensitive XAFS (X-ray Absorption Fine Structure) technique after the growth by molecular beam epitaxy (MBE). For 1ML Ge on Si(001), a rather *elongated* dimer structure with the dimer distance of 2.51A fas been observed in contrast with a Si dimer with a dimer distance of 2.25A, which indicates the dimer bond is essentially through the p-orbital overlapping. The results also show that the second-layer atoms are under the compressive strain because of the surface dimers and uniaxial mismatch strain. For 2ML Ge, we find that ~1/2ML of the second-layer Ge atoms exchanged their sites with the adjacent Si atoms under the tensile strain relaxing the strains in the second layer, which is interpreted as the first evidence for the presence of the Ge/Si interchange induced by site-selective strains.

1. INTRODUCTION

The role of heterointerface in strained-layer superlattices (SLS's) with a very short period attracts much attention in understanding their unique optical properties which are not explained by a simple zone folding scheme and a simple SLS structure. For example, the strong optical transition (0.75eV) observed for Ge_4Si_4 SLS[1] has been interpreted as an indirect transition by most of previous band calculations[2-4] based on the ordered SLS and the interface structures, however, the calculated oscillator strengths are weaker than the observed intensity by orders of magnitude. A possible superlattice structure with a relaxed bulk-like Ge-Ge distance predicts a direct transition[5] but its structural basis has been ruled out by a recent structural study[6]. More recently, the strong photoluminescence light emission at low temperature has been observed for Ge_4Si_6[7] and Ge_5Si_5[8] SLS's grown on the GeSi alloys, which attract further attention as an evidence for direct transition.

In order to understand these *exotic* optical properties of SLS's with a very short period from the microscopic viewpoints, it is important to understand the heterointerface structure, in particular, the strain localization and chemical order which strongly influence the energies of zone-folded states. The heterointerface in relation with the growth process of SLS can be directly studied by the Ge overlayers on clean Si(001) and the effect of subsequent Si growth. It is well known that the surface of Si(001) is reconstructed to form (2x1) dimer structures, stabilizing the surface by decreasing surface energy terminating dangling bonds by a dimer formation. However, the surface reconstruction introduces the additional strains within the three layers. The present paper reports the structure of Ge overlayers as a function of layer number aiming to establish the Ge dimer structure on Si(001) and the role of strain in the rearrangements of subsurface. We find that an elongated dimer structure for 1ML Ge, and for 2ML Ge, the second layer strain induced the interchange of the Ge atoms with the third layer Si atoms, in a similar manner with the strain-induced surface segregation.

2. EXPERIMENTAL

The structure of Ge epitaxial overlayers on Si(001) has been studied by *in-situ* surface-sensitive XAFS (X-ray Absorption Fine Structure) technique after the growth by molecular beam epitaxy (MBE). Ge_n overlayers (n<7) were prepared on a well-oriented p-type Si(100) (4 ohm-cm) surface and the XAFS was measured for each sample immediately after the growth. The osciilatory intensities of reflection high energy electron diffraction (RHEED) during the growth of Ge overlayers taken from the [010] azimuth were utilized to control the number of Ge layers[9].

The Ge K-EXAFS spectra for Ge on Si(001) have been obtained by detecting fluorescence using a 27-pole wiggler magnet radiation at the Photon Factory. Surface-sensitivity in the order of ~0.1ML has been achieved by a grazing incidence and a total reflection geometry. Below the critical angle, X-rays are totally refracted as they cross the interface between the two media reducing the extinction length by several orders of magnitude drastically enhancing the surface sensitivity. We have shown in a previous paper[10] that a combination of grazing incidence geometry and an energy analysis of fluorescence X-ray signal using a solid state detector can achieve the surface-sensitivity in the order of 1ML. In this work, we have used intense X-rays obtained by a multipole wiggler and a UHV-compatible 7-element Si(Li) detector. As a result, a surface sensitivity of less than 0.1ML was obtained while the effeciency of measurement was improved by more than two orders of magnitude, allowing us to appy this technique to *in-situ* studies of epitaxial layers

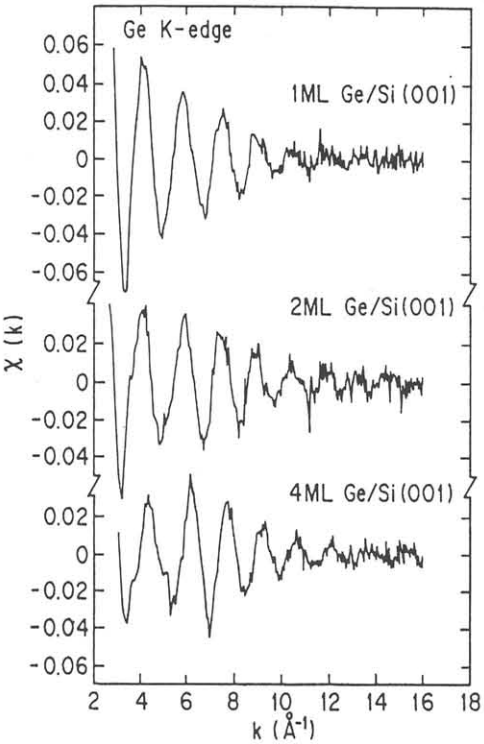

Fig. 1 Ge K-EXAFS oscillations for Ge overlayers on Si(001) as a function of photoelectron wavenumber.

on single crystal substrates[11].

3. RESULTS AND DISCUSSION

Figure 1 shows the Ge K-EXAFS oscillations for the Ge overlayers on Si(001) normalized from the fluorescence yield spectra as a function photoelectron wavenumber k. The backscattering amplitude $|f_i(\pi,k)|$ for Si peaks at low k and falls off sharply with the increase of k while $|f_i(\pi,k)|$ for Ge has a maximum at k=6-7Å^{-1} and extends to k>15Å^{-1}. The k-dependence of EXAFS oscillations indicates that the relative ratio of the Ge-Ge pair to the Ge-Si pair increases with the increase of Ge layer number n. The number of Ge-Ge and Ge-Si pairs as well as bond lengths were determined by a least-squares curve fit for various structure models taking into fact the polarization factor.

The results indicate that the 1ML Ge on Si(001) forms an *elongated* dimer structure with the average adatom-adatom distance of 2.51Å and the adatom-substrate distance of 2.40Å. Interestingly, the observed adatom-adatom distance is much longer than the reported value (2.46Å) for (2x1) Ge(001) by X-ray diffraction and interatomic distance in bulk Ge (2.45Å) inspite of the presence of uniaxial strain. According to the total energy calculation for the asymmetric dimer on (2x1) Si(001), the dimer bond is 2.25Å. It is well known that a partially ionic bonding character due to the charge transfer opens up a gap in the surface band[12]. From inspection of dimer bond length, such a charge transfer between the dimers, or the formation of asymmetric dimer is unlikely for 1ML Ge on Si(001).

Second, as shown in Fig. 2, the observed local structure of Ge dimer is quite close to the As dimers on Si(001) in both dimer bond length and adatom-substrate distance obtained by a total energy minimization[13]. This suggests that the essential feature of Ge dimer is similar with that of *elongated* As dimers with s^2p^3 configuration. The dimer bonds tend to elongate because of overlapping between the p-orbitals which are orthogonal with each other. From structural viewpoints, the elongated dimer is favorable in terms of strain energy of the subsurface layers. However, it will be shown that this will be not the case in the following. s^2p^3 configuration is possible if a charge is transferred from the substrate to the adatom. In summary, the Ge dimers on Si(001) is highlighted by an elongated p-bonding and relatively strong adatom-substrate bond. Figure 3 indicates the variation of the average Ge-Ge and Ge-Si distances as a function of Ge layer number n. In the lower column, the total energy per added Ge calculated by Tersoff[14] is also shown for comparison. We find that for n=2, the Ge-Ge distance slightly decreases while the Ge-Si distance sharrply increases to 2.42Å, where the total energy is expected to rise sharply depending on the surface strain. As shown in Fig. 3, the change at

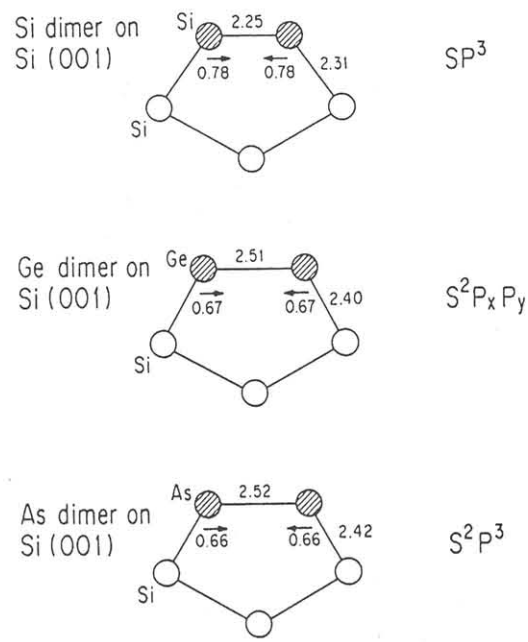

Fig. 2 Schematic of dimer structures on Si(001). The results for Si and As are based on the total energy calculation by Kruger et al.

n=2 almost completely relaxes the compressive strain in the second layer Si atoms.

The careful examination of the Ge K-EXAFS profile indicated that the site exchange between the Ge sites and Si sites. It was found that ~1/2ML of the second layer Ge atoms exchange their sites with the third layer Si atoms. This is the first direct evidence for the presence of Ge-Si site exchange for Ge overlayers on Si(001). A model structure for 2ML Ge after a site exchange is shown in Fig. 4(b). The correlated

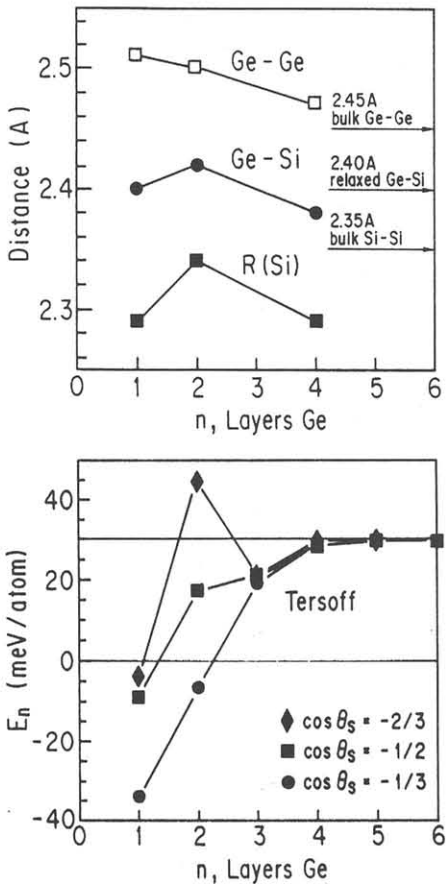

Fig. 3 The Ge-Ge and Ge-Si distances determined by a least squares analysis.

exchange between the second layer sites and the third layer sites at one side of a dimer would be stabilized with a long range order which leads to the paring of dimer and releasing of strains localized at the Ge sites. Tersoff has shown that the second layer atoms are under compression and are thus unfavorable with the Ge

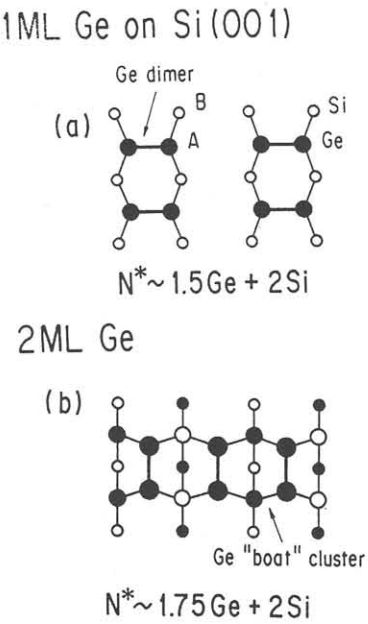

Fig. 4 Model structure for 1ML (a) and 2ML (b) Ge overlayers on Si(001).

atoms[14]. Further, the uniaxial strain due to the lattice mismatch between Ge and Si is added to the dimer-induced strain which increase the strain energy in the second layer. The strain energy is relieved by either surface segregation where the Ge atoms are stabilized on top replacing with the overgrown Si layer or the site exchange at the interface. For 2ML Ge overlayers, the latter is the only case. We find that ~1/2ML Ge atoms in the second layer indeed exchange their sites with the third layer Si atoms. The present model structure shown in Fig. 4 for 2ML Ge on Si(001) after the interchange is obtained by replacing two of the four second layer Ge atoms with the adjacent Si atoms, which are in the same row pararrel with a dimer. As a result, the two dimers tend to approach forming a dimer pair. This novel structure is expected to make both Ge-Ge and Ge-Si bonds simultaneously relax.

4. SUMMARY

The *elongated* dimer structure has been observed for 1ML Ge on Si(001), which demonstrates the Ge dimer is essentially formed by p-bonding in a similar manner with the (2x1) As on Si(001). It is found that, for 2ML Ge, about half of the second-layer Ge atoms interchange their sites with adjacent Si atoms in the third layer causing the anomalous adatom-substrate distance relaxation. Surfactant atoms can reduce the two possible mechanisms of interchange, surface segregation and site exchange at the interface by removing the strain in the second layer. However, we see almost no difference between the Ge dimers and As dimers in adatom-adatom distance but the effect on interchange is greatly different. Thus it should be noted that some electronic interaction must be considered to fully understand the site exchange phenomena, such as the electrostatic interaction due to the charge transfer between the adatom and substrate.

5. REFERENCES

1) T.P.Pearsall,J.Bevk,L.C.Feldman,J.M.Bonar and J.P.Mannaerts,Phys.Rev.Lett. 58(1987)729.
2) M.S.Hybertsoen and M.Schluter, Phys. Rev.B36,(1987)9683.
3) S.Froyen,D.M.Wood and A.Zunger, Phys. Rev.B37(1988)6893.
4) S.Satpathy,R.M.Martin and Van de Walle, Phys. Rev.B38(1988) 13237.
5) K.B.Wong,M.Jaros,I.Morrison and J.P.Hagon; Phys.Rev.Lett.60 (1988)2221.
6) H. Oyanagi, K. Sakamoto and T. Sakamoto, Jpn. J. Appl. Phys. 32 (1993) 119.
7) R. Zachai, E. Frieess, G. Abstreiter, E. Kasper and H. Kibbel, Phys. Rev. Lett. 64 (1990) 1055.
8) U. Menczigar, J. Brunner, E. Frieess, M. Gail, G. Abstreiter, H. Kibbel, H. Presting and E. Kasper, Thin Solid Films, 222 (1992) 227.
9) T.Sakamoto, H.Funabashi, K.Ohta, T.Nakagawa, N.J.Kawai and T.Kojima, Jpn. J. Appl. Phys. 23(1983)153.
10) H.Oyanagi, T.Sakamoto, K.Sakamoto, T.Matsushita,T.Yao and T.Ishiguro, J.Phys.Soc.Jpn.57 (1988) 2086.
11) H. Oyanagi, Jpn. Appl. Phys. 32 (1993) 861.
12) D.J. Chadi, J. Vac. Sci. Technolo. 16 (1979) 1290.
13) P. Kruger and J. Pollmann, Phys. Rev. B47 (1993-II) 1898.
14) J. Tersoff, Phys. Rev. B43 (1991-I) 9377.