

Strain-Induced Atomic Rearrangements in Ge Overlayers on Si(001)

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Novel features of strain-induced atomic rearrangements for germanium overlayers on Si(001) probed by surface-sensitive XAFS will be reported. The Ge adatoms form elongated dimers on Si(001) with the average Ge-Ge distance L_a of 2.51 Å, in agreement with the revised XSW results (2.55 Å). This rules out bond length shortening due to intra-dimer charge transfer predicted by LDA; there still remains a systematic discrepancy between the LDA calculations by more than 4%. The average Ge-Ge distance decreases to a relaxed bulk value L_0 (2.45 Å) for the number of Ge layers, $n = 6$, where the layer-by-layer turns into a three-dimensional growth. Two kinds of strain-induced site exchange are observed; (a) $\sim 1/2$ of Ge atoms in the second layer are replaced with Si atoms in the third layer for 2 ML Ge while (b) the Ge atoms which are placed in the second layer sites by silicon overgrowth are replaced with the first layer Si atoms. We find that the surface strain opens up a site-specific atomic migration channels, serving as a driving force of interface mixing. A microscopic mechanism of strain-induced atomic rearrangements will be discussed.

1. INTRODUCTION

For clean (2 x 1) Si(001) surface, the shortened adatom-adatom distance has been reported by both experiments [1] and total energy calculations [2]: dimers have a shorter bond length than the interatomic distance in pure bulk Si by 4-6%, suggesting a higher bond order than a sp^3 -configuration. This bond length shortening was attributed to an intra-dimer charge transfer opening an energy gap in the surface band as a result of asymmetric configuration [3]. A similar bond length contraction has been predicted for 1 monolayer (ML) Ge on Si(001) [4,5] where adatoms are uniaxially compressed because of atomic size difference between Ge and Si (4%). However, Fontes *et al.* recently reported that 1 ML Ge overlayer on Si(001) is characterized by asymmetric dimers with the anomalously long adatom-adatom distance of 2.60 Å based on the X-ray standing wave (XSW) experiment [6], in sharp contrast to 2.39 Å obtained from the energy minimization using a local density approximation (LDA) [4,5] or the sum of covalent radius 2.45 Å.

The extended X-ray absorption fine structure (EXAFS) technique has been recognized as a powerful probe of local structure which can directly and precisely measure the adatom-adatom bond length. The local structure of Ge overlayers on Si(001) has been studied by Surface-sensitive EXAFS based on a grazing-incidence fluorescence detection. The results clearly evidenced the elongated

dimer configuration and ruled out a shortened dimer model [4,5]. The local structure of Ge dimers suggests that adatoms take the p^3 -like configuration. Possibility of a substrate-to-adatom charge transfer is discussed in relation to the dimer configuration and surface stress.

2. EXPERIMENT

The structure of Ge epitaxial overlayers on Si(001) has been studied *in situ* after the growth using the molecular beam epitaxy (MBE) technique. A 1.6 mm thick disk-shaped undoped Si(001) substrate with a diameter of 22 mm was chemically cleaned by the Shiraki method prior to the insertion to the vacuum. The Ge_n overlayers ($n < 7$) were prepared on well-oriented Si(001) surfaces at 400 °C in a MBE growth chamber with a base pressure of 1×10^{-10} Torr which is connected to the main analysis chamber. The oscillatory 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 [7]. For clean (2 x 1) Si(001) surface, the oscillation of RHEED intensity sharply decreases with the coverage above 6 MLs indicating that the growth mode changes from a two-dimensional to a three-dimensional one. The sample was transferred to the analysis chamber with a base pressure of 5×10^{-11} Torr immediately after the growth without breaking the vacuum. The main

analysis chamber is connected to an MBE chamber through a preparation chamber which are separately evacuated by 400l/sec ion pump. Samples can be transferred between these three chambers on a transporter. Comparing RHEED patterns taken before and after the XAFS measurement with that taken during the growth, it was confirmed that the surface structure was preserved.

3. RESULTS AND DISCUSSION

Adatom dimers are formed on Si(001) by the surface reconstruction with a (2x1) ordered structure which stabilize the unreconstructed surface reducing the number of dangling bonds at the sacrifice of surface strain energy. The symmetry of dimers which still remains controversial is strongly related with the surface electronic band structure. An asymmetric configuration leads to a direct surface-state gap while a symmetric one results in a metallic or semimetallic surface band [2,3]. Total energy calculations indicated that the dimer bond length would be shortened for an asymmetric configuration because of a charge transfer from a lower adatom to an upper adatom. The adatom-adatom bond length 2.25 Å calculated for an asymmetric dimer configuration for (2x1) Si(001) is indeed shorter than the interatomic spacing in bulk Si (2.35 Å) by 4.4% [4], which has been confirmed by the recent transmission electron diffraction experiment [1].

The results for 1 ML Ge on Si(001) summarized in Table I indicated that the Ge adatoms form *elongated dimers* with the average Ge-Ge distance L_a of 2.51 ± 0.04 Å, in significant contrast to the shortened adatom-adatom bond length for clean (2x1) Si(001). This contradicts a simple expectation that L_a is shorter than the interatomic distance in Ge (L_0 , 2.45 Å) because of uniaxial stress due to the 4% atomic size mismatch between Ge and Si, and the ionic bonding character if the asymmetric configuration is formed. The observed L_a is substantially longer than the reported value (2.44 Å) for (2x1) Ge(001) by a surface X-ray diffraction [8] or L_0 . On the other hand, the adatom-substrate distance coincided with the sum of covalent radius (2.40 Å). The observed adatom-substrate distance (L_s) 2.40 ± 0.08 Å indicates a contraction of the substrate Si atom by the same amount (-2.4%). A relative change of the bond length ratio $\Delta\alpha = L_a/L_0 - 1$ takes a negative value for epitaxial layers under uniaxial compressive strain: the Ge-Ge distance in

strained GeSi alloys on Si(001) is 2.42 Å ($\Delta\alpha = -0.012$) in contrast to 1 ML Ge overlayer ($\Delta\alpha = 0.025$).

Discrepancy between the experiment [6] and the total energy calculation [4] on the Ge dimer bond length on Si(001) has been a subject of intense discussion. Kruger *et al.* claimed that the optimization gives a reliable bond length since $L_a = 2.41$ Å for clean (2 x 1) Ge(001) is in good agreement with the X-ray result ($L_a = 2.44$ Å), taking into account the fact that the energy minimization within a framework of LDA approach gives slightly shorter bond length by 1 %. Our results indicate that the elongation of dimer bond length reported by Fontes *et al.* is essentially correct. However, $L_a = 2.60$ Å determined by XSW was considerably overestimated. Interestingly, $L_a = 2.51$ Å coincides with the calculated dimer bond length using a (4x2) unit cell. We note, however, that the calculated bond length for a (4x2) unit cell is longer than those based on a (2x1) symmetry [4,5] showing that the dimer bond length is strongly dependent on the long-range interaction between dimers or the effects of surface stress extending over several dimer units.

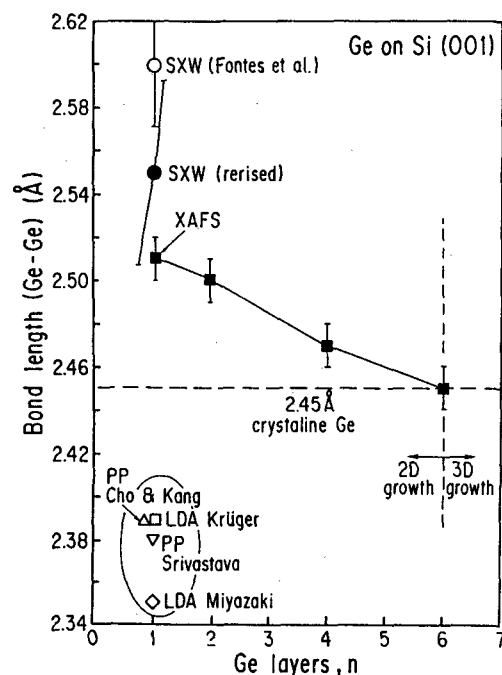


Fig. 1 Ge-Ge distances for the Ge overlayers on Si(001).

The agreement between $k\chi(k)$ simulated for a short asymmetric dimer model [4] and the experimental data is poor. The disagreement in the phase of sinusoidal oscillation is due to the underestimation L_a . This clearly rules out a possible model [4]. For an elongated dimer configuration, $k\chi(k)$ was simulated for the modified model in which L_s (2.40 Å) is conserved. Although the modified model gave a better fit to the experimental data, the frequency of $2kr$ oscillations is still considerably lower. This shows that the L_a in this model is overestimated indicating improper structural constraints, *i.e.*, the conserved center of mass in ref. 6.

The essential feature of the present results is that both L_a and L_s are quite similar to those observed for symmetric As dimers on Si(001). It is reasonable to observe that group V element adatoms take a symmetric configuration compatible with the s^2p^3 bonding. This has been confirmed by total energy calculations [7,8]. The anomalous elongation of dimer bond found for 1 ML Ge on Si(001) suggests a p -like character in the surface band. Buckling of dimer bond modifies the in-plane component of polarization factor as a function of $\cos^2\theta$, which modifies the magnitude of $\chi(k)$ by less than 10%. Equal amount of domains with parallel and perpendicular dimer orientations coexist in single-step double-domain Si(001) surface. If the in-plane components for "up" and "down" atoms in the two domains parallel and perpendicular dimer orientations are averaged out, the overall in-plane polarization factor becomes unity and independent on the polarization direction, which leads to constant $N^*S_i = 2.0$.

The elongated dimer configuration is interpreted in terms of s^2p^3 -like configuration. A possible driving force of such a charge transfer might be the surface strain: bending of adatom-substrate bonds would induce the electron transfer. Indeed, the elongation of a dimer bond due to a charge transfer has been reported. Mangat *et al.* have observed that the shortened Si-Si distance (2.20 Å) is elongated to 2.44 Å changing the configuration from asymmetric to symmetric when 1 ML Na is adsorbed [9].

In a dynamical picture, the time-average of the two equivalent positions of asymmetric dimers is observed as a symmetric dimer. The low-temperature STM image of (2x1) Si(001) showed that asymmetric dimers predominate in the defect-free regions at 120 K while at room temperature a

symmetric dimers are observed [10]. For 0.1-0.2 ML Ge on Si(001), Iwawaki *et al.* observed a symmetric STM image at room temperature [11]. Since the flipping rate is much higher than a time scale of STM, this could lead to a symmetric STM image as a time-averaged quantity. However, since the time scale of X-ray absorption or photoemission is in the order of 10^{-15} sec., the observation of elongated dimer by SEXAFS is not interpreted as a time-average structure. A dynamical flipping mechanism can not explain the elongated Ge dimers on Si(001).

4. CONCLUSION

The structure of Ge dimers on well-oriented Si(001) has been studied by surface-sensitive XAFS technique using a grazing-incidence fluorescence detection and a 27-pole wiggler. The bond length values for adatom-adatom and adatom-substrate pairs were determined from the Ge K-EXAFS. For 1 ML Ge on Si(001), the elongated Ge dimer structure with the Ge-Ge bond length of 2.51 ± 0.04 Å was observed. The observed local structure around Ge atoms indicates that the adatoms take the p^3 -like configuration commonly observed for symmetric dimers. The results suggest that a substrate-to-

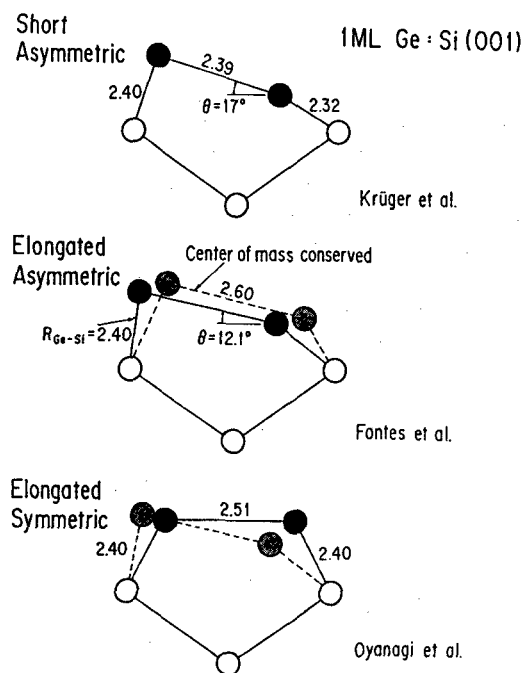


Fig. 2 Model structures for 1 ML Ge dimers on Si(001).

Table I. Bond lengths for adsorbed elements on Si(001).

System	Bond length (L_a)	L_a/L_0 (α)	$\Delta\alpha$	Reference
Si(001)	2.18 Å	0.928	-0.072	ref. 1
	2.25 Å	0.957	-0.043	ref. 4
Ge(001)	2.44 Å	~1.0	~0	ref. 19
Ge/Si(001)	2.51 ± 0.04 Å	1.024	+0.024	this work
Na/Si(001)	2.44 Å	1.04	+0.04	ref. 24

* L_a is a bond length between adatom and substrate.

** L_0 is a bond length in pure bulk material.

adatom charge transfer is induced by surface strain. It was demonstrated that the surface-sensitive XAFS technique based on a grazing-incidence fluorescence detection has submonolayer sensitivity in a hard X-ray region.

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