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Determination of a p(3√2×√2)*R*45° Structure Formed by Sn Adsorption on Cu(001): A Tensor Low-energy Electron Diffraction Analysis

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Low-energy electron diffraction (LEED) have been used to determine the p(3√2×√2)*R*45° structure formed at 300 K by adsorption of Sn atoms on Cu(001). It is confirmed that the same model suggested by previous studies of surface x-ray diffraction, density functional calculations and LEED analysis is correct. It contains missing-rows along the [100] direction. Optimum parameters of the p(3√2×√2)*R*45° structure reveal that the substitutional Sn atoms laterally displaced by 0.30 ± 0.05 Å away from ideal fourfold-hollow sites. Distance between the nearest-neighbor substitutional Sn atoms is 3.02 ± 0.05 Å, suggesting the formation of an Sn dimer. The stabilization mechanism of the p(3√2×√2)*R*45° structure is discussed.

1. Introduction

It has been demonstrated that various ordered surface structures are formed on the Cu(001) surface by adsorption of metals at room or slightly higher temperatures[1,2]. Among such adsorption systems, Sn-adsorbed Cu(001) surfaces are extensively studied[3-15]. The Cu(001)-Sn system showed five ordered phases at room temperature in a submonolayer coverage[8,13]. The first ordered phase is a "p(2×2)" structure formed at Sn coverage of about 0.2 monolayer (ML). The coverage is defined as the ratio of surface density of adsorbed metal atoms with respect to that of the ideal surface Cu atoms. Sn atoms are located at substitutional sites and form a local p(2×2) structure with anti-phase domains[5]. With increasing coverage, a p(2×6) structure is formed at 0.33 ML. Diffraction patterns of the p(2×6) structure have missing spots, that is, glide planes are present[10]. Subsequently observed phase is a c(4×8) structure, that was discovered recently by scanning tunneling microscopy (STM) studies[9,10]. The coverage of a proposed model is 0.375 ML. At 0.5 ML, a p(3√2×√2) *R*45° structure is formed. This structure was determined by several methods including a low-energy electron diffraction (LEED) intensity-voltage (*I-V*) analysis. A half of surface Cu atoms are substituted by Sn atoms and a sixth of surface Cu atoms are removed leaving vacancies. The vacancies are assembled to be single missing-rows along the [100] direction[6]. Very recently, a double missing-row structure has been locally observed by STM[15]. In addition, a reversible phase transition between the p(3√2×√2)*R*45° and a c(2×2) structure at 360 K was observed[7]. The high-temperature phase is the c(2×2). Upon further deposition of Sn, a c(4×4) structure is observed at about 0.65 ML and an overlayer model was proposed[3]. Recently, a new structure model was proposed from STM observations[10,13]. It was suggested that the c(4×4) structure consists of one substitutional Sn atom and four Sn adatoms per unit cell.

In the present paper, we report a reinvestigation of the p(3√2×√2)*R*45° structure using LEED *I-V* analysis. The determined structure is the same model suggested by previous LEED study[6]. However, the structural parameters are quite different. We discuss the stabilization mechanism of the p(3√2×√2)*R*45° structure.

2. Experiment and Calculation

The experiments were carried out in an ultra-high vacuum (UHV) chamber equipped with a commercial LEED optics. The base pressure in the UHV chamber is less than 4×10^{-10} Torr during experiments. The Cu(001) surface was cleaned by repeated cycles of argon ion bombardment (0.5 keV, 1.5 μA) and subsequent annealing to 800 K. Sn atoms were evaporated from a home-made Knudsen cell onto Cu(001) at 300 K. LEED spot intensities for *I-V* curves were recorded by a computer-controlled video LEED system at a sample temperature of 130 K. Details of the experiment were similar to the previous study[16].

A Barbieri/Van Hove symmetrized automated tensor LEED package was used to calculate *I-V* curves for structure models[17]. The programs searched for agreement with the experiment by minimizing the Pendry *R*-factor, R_p[18]. The real part of inner potential was determined during the course of the theory-experiment fit. The damping was represented by an imaginary part of the potential, V_{oi}, of –5.0 eV. The error range of structural parameters were obtained from the variance of R_p[18], $\Delta R = R_{min}\ (8\ |V_{oi}|\ /\ \Delta E)^{1/2}$, where Rmin is the minimum Rp factor achieved and ΔE is the total energy range of measured *I-V* curves for in-equivalent spots.

3. Results

The p(3√2×√2)*R*45° structure was previously investigated by some experimental methods[3,4,10,14,15] including a LEED *I-V* analysis[6]. We consider that the optimized value of the R_p of 0.26 obtained in the previous LEED analysis[6] is relatively large in spite of large number of structural parameters (five complete Cu layers are included in the optimization). Here, we have

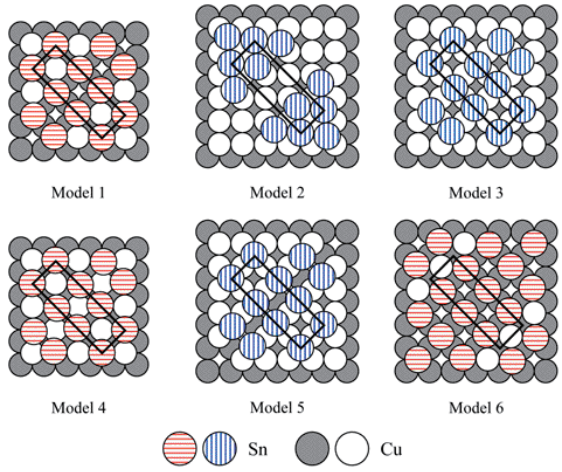

Fig. 1 Ball models of examined 6 structures of Cu(001)-p(3√2×√2)*R*45°-Sn (top view).

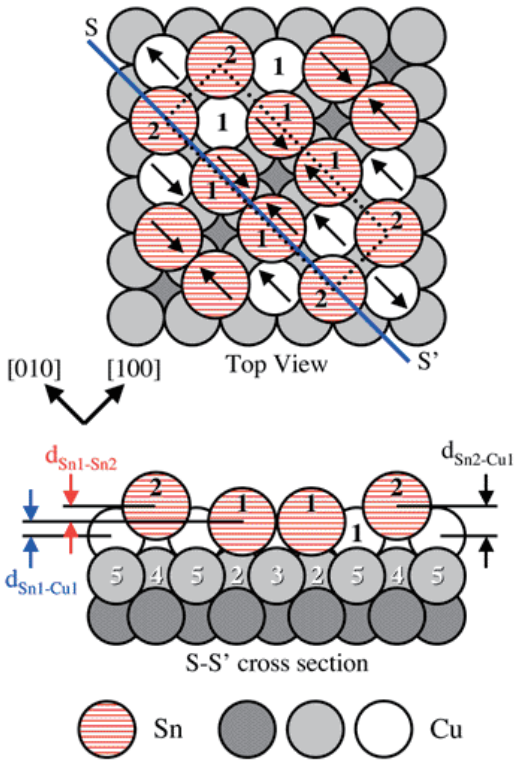

Fig. 2 Top and cross sectional views of the Cu(001)-p(3√2×√2)*R*45°-Sn structure.

reinvestigated this structure using a tensor LEED *I-V* analysis, because we have obtained a rather large range of the total energy of 3977 eV for inequivalent beams (2280 eV in the previous study[6]). Six examined structure models are shown in Fig. 1: surface alloy with single missing-row model by Pussi *et al.*[6] (model 1); overlayer model by Argile *et al.*[3] (model 2); overlayer and surface alloy models by McLoughlin *et al.*[4] (models 3 and 4); overlayer with subsurface missing-row model by Lallo *et al.*[10] (model 5); and surface alloy with double missing-row model by Fuhr *et al.*[15] (model 6). We have obtained a very good R_p value of 0.12 for optimized model 1 under the condition of the same number of structural parameters as Ref. 6. The R_p of other five models gave above 0.31. The value of 0.31 is large enough to be excluded, because the error range of the R_p of the present study is only 0.01. Thus, we have confirmed model 1 is correct. Optimized Debye temperatures for Sn, surface Cu and other Cu atoms were 140, 240 and 343 K, respectively.

Top and cross sectional views of best-fit structure (model 1) are illustrated in Fig. 2. The numbers identify equivalent atoms. Arrows indicate directions of lateral displacements of Sn1 and Cu1 atoms from fourfold-hollow sites in the second layer. Sn2 atom is not allowed to displace laterally due to the symmetry requirement. Optimized parameters are summarized in Table 1. Lateral displacement and height difference are listed in Table 2 and 3, respectively, in which our results are compared with those in the previous LEED[6], surface X-ray diffraction (SXRD)[14] and DFT[15] studies. The error ranges were obtained from the variance of the R_p mentioned above[18], and they were much smaller, on the whole, than those in Ref. 6. Comparison of our *I-V* curves between of experiment and of theoretical best-fit structure is depicted in Fig. 3. The agreement is very good.

4. Discussion

First, we compare our optimized values of structural

Table 1 Structural parameters for optimized structure in Fig. 2

Atom	Displacement along arrow (Å)	Height (Å)
Sn1	0.30 ± 0.05	9.37 ± 0.02
Sn2	-	9.43 ± 0.03
Cu1	0.17 ± 0.05	9.06 ± 0.01
Cu2	0.06 ± 0.05	7.19 ± 0.02
Cu3	-	7.11 ± 0.03
Cu4	0.03 ± 0.06	7.23 ± 0.02
Cu5	-	7.27 ± 0.02

Table 2 Lateral displacements of Sn1 and Cu1 atoms in the Cu(001)-p(3√2×√2)*R*45°-Sn structure. Corresponding atoms are indicated in Fig. 2

Atom	Displacement along arrow (Å)			
	LEED [6]	SXRD [14]	DFT [15]	this study
Sn1	0.26 ± 0.10	0.27 ± 0.01	0.26	0.30 ± 0.05
Cu1	0.01 ± 0.04	0.15 ± 0.03	0.13	0.17 ± 0.05

Table 3 The rumplings of Sn-Sn and Sn-Cu in the Cu(001)-p(3√2×√2)*R*45°-Sn structure compared with Ref. 6, 14, and 15 shown in Fig. 2

rumpling	Value (Å)			
	LEED [6]	SXRD [14]	DFT [15]	this study
$d_{Sn1-Sn2}$	0.12 ± 0.08	0.13 ± 0.03	0.12	0.06 ± 0.03
$d_{Sn1-Cu1}$	0.27 ± 0.07	0.22 ± 0.02	0.41	0.31 ± 0.02
$d_{Sn2-Cu1}$	0.39 ± 0.07	0.35 ± 0.03	0.53	0.37 ± 0.02

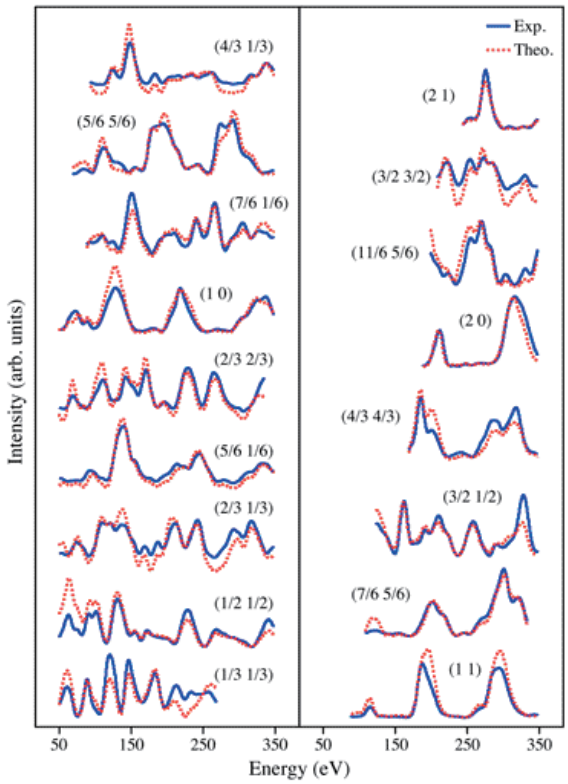

Fig. 3 Comparison between the experimental (solid line) and best-fit theoretical (dashed line) *I-V* curves for Cu(001)-p(3√2×√2)*R*45°-Sn.

parameters with those obtained by the previous LEED[6], SXRD[14] and DFT[15] studies. Table 2 is one of such comparisons for lateral displacements of Sn1 and Cu1 in Fig. 2, while Table 3 for height differences among surface atoms of Sn1, Sn2 and Cu1. In both tables our values are obtained from Table 1. Bond distances such as Sn1-Sn1 are obtained also from Table 1. In Table 2, values of the displacement of Sn1 are very similar in four studies[6,14,15]. On the other hand, previous studies reported considerably different values for Cu1. SXRD[14] and DFT[15] studies show relatively large displacements but the previous LEED study[6] concluded almost no displacement. Our LEED study confirms that Cu1 atoms laterally displace considerably from the hollow sites.

Second, we discuss features of the p(3√2×√2)*R*45° structure on the basis of structural parameters obtained in this study. This structure is a new type of surface ordered alloys. Basically it may be classified into the c(2×2) check-like surface alloys. However, there is a big difference: Every third Cu atoms at the surface are completely removed away along [100] directions induced by Sn adsorption. In the removed area, pairs of Sn atoms are aligned along the [100] directions (see Fig. 2). The bond distance of the paired Sn atoms is obtained to be 3.02 ± 0.05 Å (see Table 3), suggesting the formation of Sn dimers. The nearest Sn atom distance in β-tin is 3.016 Å[19]. The dimers are arranged like dimer-rows along the [100] directions, but it is noted that the distance between neighboring dimers is 3.61 Å, indicating there are little direct chemical bonds.

Finally, we discuss the origin of the stabilization of the p(3√2×√2)*R*45° structure. The formation of Sn dimers becomes possible by removing surface Cu atoms along the [100] direction. This suggests that the dimer formation results in a considerable gain of the adsorption energy at the cost of surface vacancy formation energy. The coverage of surface Cu vacancies is 2/3 ML in the p(3√2×√2)*R*45° structure, while 1/2 ML in the c(2×2) structure. The dimer formation provides an additional gain of the adsorption energy: Surface Cu (Cu1 in Fig. 2) atoms can displace away from Sn2 atoms to allow Sn2 atoms go down deeper. Then, Sn2 atoms become possible to interact with the second layer Cu atoms more effectively. Thus, the p(3√2×√2)*R*45° structure stabilizes more than the c(2×2) substitutional structure. The DFT calculations[15] conclude that the p(3√2×√2)*R*45° structure is more stable than the c(2×2) substitutional structure by 90 meV/Sn atom: The adsorption energy of Sn atom in the former is 4.03 eV, while that in the latter is 3.94 eV.

5. Summary

Sn adsorbed Cu(001) surface has been studied by LEED at room temperature. We succeeded the determination of p(3√2×√2)*R*45° structure by the tensor LEED *I-V* analysis. Our result showed a previously suggested structure that contains single missing-row along [100] direction is correct. Large lateral displacements of Sn1 and Cu1 atoms from ideal fourfold-hollow sites in Fig. 2 are observed. Sn1 atoms are stabilized by formation of dimers to gain an additional adsorption energy.

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