The structural analysis of Cu(111)-Te $\left(\sqrt{3} \times \sqrt{3}\right)$R30° and $\left(2\sqrt{3} \times 2\sqrt{3}\right)$R30° surface phases by quantitative LEED and DFT

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ABSTRACT

The chemisorption of tellurium on atomically clean Cu(111) surface has been studied under ultra-high vacuum conditions. At room temperature, the initial stage of growth was an ordered $\left(2\sqrt{3} \times 2\sqrt{3}\right)$R30° phase (0.08 ML). An ordered $\left(\sqrt{3} \times \sqrt{3}\right)$R30° phase is formed at 0.33 ML coverage of Te. The adsorption sites of the Te atoms on the Cu(111) surface at 0.08 ML and 0.33 ML coverages are explored by quantitative low energy electron diffraction (LEED) and density functional theory (DFT). Our results indicate that substitutional surface alloy formation starts at very low coverages.

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1. Introduction

After decades of research, the adsorption of Te on copper remains interesting because of its technological importance. A crucial component of a solar cell is its back contact which is typically made of CuTe [1]. The efficiency of a solar cell can be increased through the back-contact, by controlling the doping amount of Te into Cu. In addition to the application in solar cell industry, the complexity and the richness of the alloy phases of this material [2,3] and the ability to tune the electronic properties by altering relative composition, makes CuTe attractive for scientific research.

Even though a number of studies have been done on polycrystalline copper telluride system [4–8], studies on the gas phase deposition of Te on a low index, single Cu(111) crystal are limited. An early, off normal, low energy electron diffraction study [9] mentioned the formation of well ordered $\left(2\sqrt{3} \times 2\sqrt{3}\right)$R30° phase at the very low coverage of Te (0.08 ML). According to this experiment, the Te atoms chemisorped on the underlying Cu(111) surface, occupying a single bridge position, between two below-lying Cu atoms. In contrast, later, the result from a SEXAFS study [10] on this system, indicated the possibility of surface substitutional alloy formation.

A recent, more detailed characterization of growth of Te on Cu(111) surface [11] by vapor deposition, confirmed the appearance of the $\left(2\sqrt{3} \times 2\sqrt{3}\right)$R30° LEED spots at ~0.08 ML. The spots were reported to be sharpest around 0.17 ML coverage of Te. After that, the LEED spots progressively became diffuse with an increase of Te coverage up to 0.3 ML. The combined STM, XPS and UPS studies on this phase concluded the direct incorporation of the Te atoms in the surface plane of Cu(111) which supported the surface alloying suggested earlier [10]. A $\left(\sqrt{3} \times \sqrt{3}\right)$R30° LEED structure was observed with further deposition of Te up to 0.68 ML, at room temperature. Initially, this phase remained disordered. The LEED spots became sharp after annealing at about 300 °C for 5 min, at a Te coverage around 0.25 ML. Similar to the low coverage $\left(2\sqrt{3} \times 2\sqrt{3}\right)$ phase, the results from STM and XPS studies indicate the surface substitutional surface alloy formation for the $\left(\sqrt{3} \times \sqrt{3}\right)$R30° structure. However, the alloying was restricted to the uppermost (111) layer. At high coverage, >0.69 ML of Te, the $\left(\sqrt{3} \times \sqrt{3}\right)$R30° pattern retained its symmetry but STM measurement revealed a ~3.2% in plane lattice contraction with respect to the lower coverage structures. The binding energies of the Cu 2p and Te 3d spectra, attributed to the surface substitutional alloy phase in case of $\left(\sqrt{3} \times \sqrt{3}\right)$R30° were absent. Thus, based on the observation of both the XPS and STM experiments, a complete formation of an ordered Cu_3Te_2-like alloy phase was proposed.

Tellurium atomic layers, formed by evaporative deposition in vacuum, on other fcc(111) metal surfaces have been studied by a variety of different surface sensitive techniques. LEED studies of Te on Ni(111)
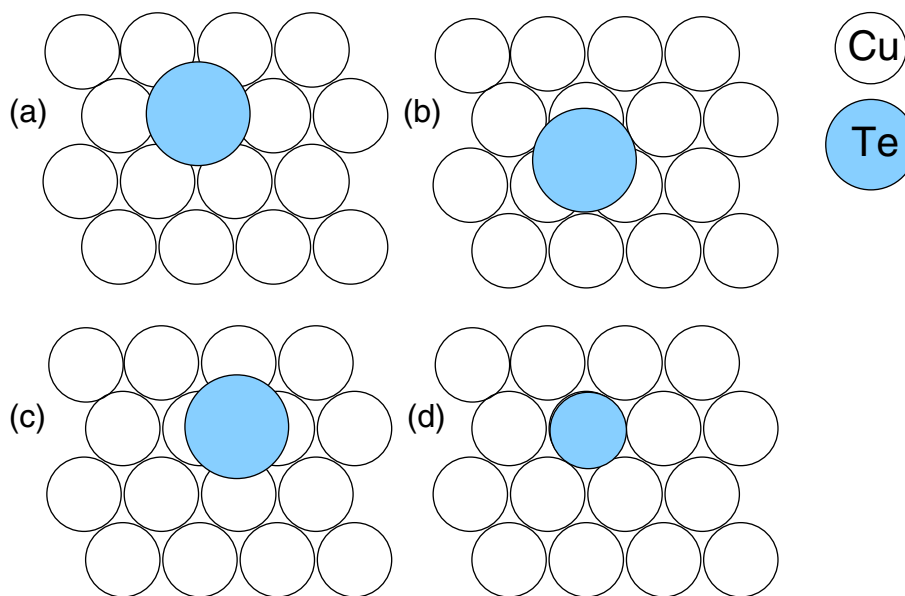

Fig. 1. Top views of the adsorption sites used in LEED and DFT analysis. (a) Top site. (b) Hollow site. In hcp hollow there is an atom in the second substrate layer just below the adsorbate and in fcc hollow the next atom below the adsorbate is in the third substrate layer. (c) Bridge site. (d) Surface alloy. Only the top layer copper atoms are shown.

reported a $\left(2\sqrt{3} \times 2\sqrt{3}\right)R30°$, $\left(\sqrt{3} \times \sqrt{3}\right)R30°$, and complex patterns [12,13]. Angular resolved photoemission studies of the Ni(111)-$\left(\sqrt{3} \times \sqrt{3}\right)R30°$ suggested that Te atoms in this structure are bound in threefold hollow sites [14–16]. On Au(111) LEED results show that the first monolayer of Te is arranged with an incommensurate Au(111)-$\left(\sqrt{3} \times \sqrt{3}\right)R30°$-Te structure, and after the completion of the first monolayer, a (3×3)-Te structure appears [17]. In $\left(\sqrt{3} \times \sqrt{3}\right)$ R30° phase the adatoms are believed to occupy the three-fold hollow sites of the underlying Au(111) substrates [18].

Antimony, which is next to the tellurium in the periodic table, has been studied on Ag(111) and Cu(111) surfaces [19]. For both substrates at coverages below 0.33 ML, the Sb atoms are embedded randomly into the surface layer, forming a substitutional surface alloy. A sudden formation of $\left(\sqrt{3} \times \sqrt{3}\right)R30°$ stacking fault alloy is reported when the coverage becomes near 0.33 ML [19]. Medium energy ion scattering measurements performed on Cu(111)-$\left(\sqrt{3} \times \sqrt{3}\right)R30°$-Sb [20] are found to be consistent with the stacking fault position proposed by de Vries et al. [19]. The driving force for this reconstruction is proposed to be the repulsive interaction between Sb atoms [19].

In this paper we present a detailed analysis of the structures of the 0.08 ML and 0.33 ML phases of Te on Cu(111) surface by quantitative LEED and DFT.
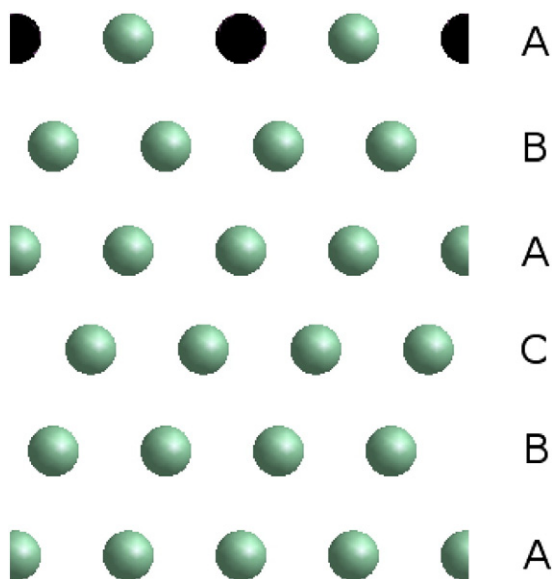
2. Experiment

The experiments were carried out in a standard ultra high vacuum (UHV) chamber equipped with a rear-view LEED optics from OCI Vacuum Microengineering and an electron energy analyzer with dual anode X-ray source from PSP Vacuum Technology. The chamber has been

Fig. 2. Side view for the faulted alloy structure for $\left(\sqrt{3} \times \sqrt{3}\right)R30°$ phase. The capital letters represent the ABC-stacking for fcc(111) surface. Black atoms are tellurium and green atoms are copper.

Table 1
Pendry R-factors for different structures for $\left(2\sqrt{3} \times 2\sqrt{3}\right)$-phase and $\left(\sqrt{3} \times \sqrt{3}\right)$ phase. The last line shows the Pendry variance. The values with bold font are the values that fit inside the Pendry variance and thus are possible structures.

Geometry	Pendry R-factor $\left(2\sqrt{3} \times 2\sqrt{3}\right)$	Pendry R-factor $\left(\sqrt{3} \times \sqrt{3}\right)$
Top	0.26	0.70
Fcc hollow	0.29	0.67
Hcp hollow	**0.22**	**0.36**
Bridge	0.59	0.54
Alloy	**0.24**	0.54
Faulted alloy	0.48	**0.41**
Variance	0.03	0.06