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Growth and alloying of thin film Te on Cu(111)

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ABSTRACT

We explore the growth and temperature-dependent alloying of Te on Cu(111) using a combination of low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) and scanning tunnelling microscopy (STM). Below 275 K, growth is rough and disordered. Above 275 K, there are two distinct surface phases: a surface substitutional alloy for coverages below 0.33 ML and a Cu_3Te_2-like alloy above 0.66 ML, with the phases coexisting at intermediate coverages. The alloy is consistent with the (111)-termination of an unusual phase with $F\bar{4}3m$-symmetry that is well lattice-matched to the underlying Cu(111). It is relaxed and incommensurate, showing a long-range periodicity consistent with a floating overlayer.

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1. Introduction

Copper telluride alloys form an important but understudied component of several high efficiency CdTe thin film photovoltaics: either explicitly or as a consequence of interfacial reactions between the active layer and underlying Cu-based contacts [1–6]. A critical aspect of photovoltaic production is the reliable formation of a pseudo-ohmic back contact [7,8]; yet copper tellurides exist in a multitude of phases, giving rise to substantial variability in device performance and stability [4]. This problem has motivated several recent studies [9–13] of typically polycrystalline systems, which tend to conclude with the assignment of Cu_2Te formation, albeit spanning a broad range of non-stoichiometric $Cu_{2-x}Te$ compounds after heating. In contrast, there are limited previous studies of Te deposition onto single crystal Cu(111). An early low energy electron diffraction (LEED) study [14] was interpreted as showing related $(2\sqrt{3} \times 2\sqrt{3})$ R30° and $(\sqrt{3} \times \sqrt{3})$ R30° unalloyed overlayers at Te coverages (θ_{Te}) of 0.08 and 0.33 monolayers (ML), respectively. Surface extended X-ray absorption fine structure (SEXAFS) analysis [15] later indicated that these structures were surface substitutional alloys (SSAs), with Te atoms sitting only 0.84 Å above the Cu nuclear plane. The LEED study also suggested epitaxial growth of thicker Te(0001) overlayers at room temperature, although alloying would be expected from a thermodynamic perspective. Alloying of thicker Te films on single crystal Cu(111) has, to our knowledge, not been explored, despite the obvious technological motivation to understand device behaviour during

thermal processing. We address this issue here. We present a detailed characterisation of the initial growth of Te on single-crystal Cu(111) and show immediate surface alloying at temperatures above 275 K. Continued Te deposition leads to the formation of a stable alloy phase that is consistent with a relatively unusual bulk Cu_3Te_2-like alloy with $F\bar{4}3m$ symmetry. Our study provides insight into the fundamentals of Te/Cu(111) growth and alloying, thereby aiding the interpretation of device performance in more applied studies.

2. Experimental

X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), low energy electron diffraction (LEED) and scanning tunnelling microscopy (STM) measurements were performed in two separate ultra-high vacuum (UHV) systems, both with a base pressure of 2×10^{-10} mbar. The first chamber was equipped with a LEED optic in addition to a He(I) discharge lamp and an Al K_α X-ray source for UPS and XPS, respectively. Spectra were collected at normal emission using a concentric hemispherical analyzer (CLAM2, VG Ltd.). The second chamber was used primarily to collect STM data but also had LEED and XPS capabilities that were used for coverage calibration. STM images were obtained using an Omicron STM-1 instrument with MATRIX software, using an electrochemically etched W tip and in constant current mode. The Cu(111) sample was cleaned in-situ by repeated cycles of Ar^+ bombardment (1 kV, ~8 μA cm^{-2}, 30 min) and annealing (830 K, 30 min). Sample cleanliness and crystallinity were verified in both systems by XPS and LEED. The substrate temperature was controlled using a combination of liquid nitrogen cooling and radiative heating to achieve temperatures between 120 K and 300 K. Above room temperature the substrate was annealed using an e-beam heater. For the

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annealing experiments of Section 3.4, data were collected at 120 K, following incremental anneals where the sample was held for 10 min at successively higher temperatures, then cooled. Te was deposited from a homemade effusion cell held at 570 K. The deposition rate for sub-monolayer films was calculated to be ~0.2 ML min^{-1} using Cu 2p$^{3/2}$ and Te 3d$^{5/2}$ XPS data and known cross sections [16–18]. For film thicknesses greater than 10 ML, the effusion cell was held at 610 K to give a deposition rate of ~5 ML min^{-1}. All coverages quoted here have an estimated error of ±0.05 ML and we define 1 ML as being the number of atoms in the ideal Cu(111) surface plane.

3. Results and discussion

3.1. Low coverage regime: $0 < \theta_{Te} < 0.33$ ML

Room temperature (300 K) deposition of Te was first monitored by LEED, as shown in Fig. 1, and is in good agreement with the literature [14]. The dashed lines in Fig. 1 demarcate the first Brillouin zone of the clean Cu(111) surface and all images were collected at the same energy to aid comparison. The first ordered pattern has $(2\sqrt{3} \times 2\sqrt{3})$ R30° symmetry and appears at 0.08 ML but is sharpest around $\theta_{Te} \approx 0.17$ ML, then becomes progressively more diffuse up to ~0.3 ML. Measurement of diffraction spot positions indicate that the surface lattice vector has expanded by ~2.8% with respect to the clean Cu(111) surface (i.e. to 2.63 Å), which could indicate strain arising from direct incorporation of Te into the surface plane. Interestingly, and

in spite of the increased Te incorporation, the apparent lattice constant is invariant between Te coverages of 0.08 ML and 0.33 ML.

Surface alloying was confirmed by complementary Te 3d$^{5/2}$ and Cu 2p$^{3/2}$ XPS data, collected immediately after LEED analysis and presented in the first panels of Fig. 2. Each spectrum was fitted to the product of a Gaussian and a Doniach–Sunjic [19] function and the fitted binding energies, presented in Table 1, are in agreement with previous studies of copper and tellurium systems [20–23]. Reference spectra were collected from the clean Cu(111) surface (upper right panel of Fig. 2) and a thick, 22 ML Te film that was deposited and measured below the alloying transition temperature (upper left panel of Fig. 2). For each fit, peak widths were fixed to those of the reference spectra whilst the asymmetries were free parameters and were fitted to yield results that are consistent with previous observations of Cu and other p-block semi-metals (e.g. Sn [23]). Specifically, we obtain asymmetry values $\alpha_{Cu} = 0.02$ and $\alpha_{Te} = 0.12$, using the definitions of Ref. [19]. For a coverage of 0.18 ML, the Te 3d$^{5/2}$ data are well fitted by a single component of 572.3 eV binding energy, which is 0.8 eV lower than the value we measured for elemental Te. The Cu 2p$^{3/2}$ data can be fitted by two components: the largest is identical to the Cu reference and corresponds to bulk Cu, at 932.4 eV; a smaller component, shifted by 0.2 eV to higher binding energy, indicates slight charge transfer away from the surface Cu atoms. Thus, our data suggest that the $(2\sqrt{3} \times 2\sqrt{3})$ R30° surface contains a single Te$^{\delta-}$ species and a minority Cu$^{\delta+}$ species (where δ refers to a partial transfer of charge)
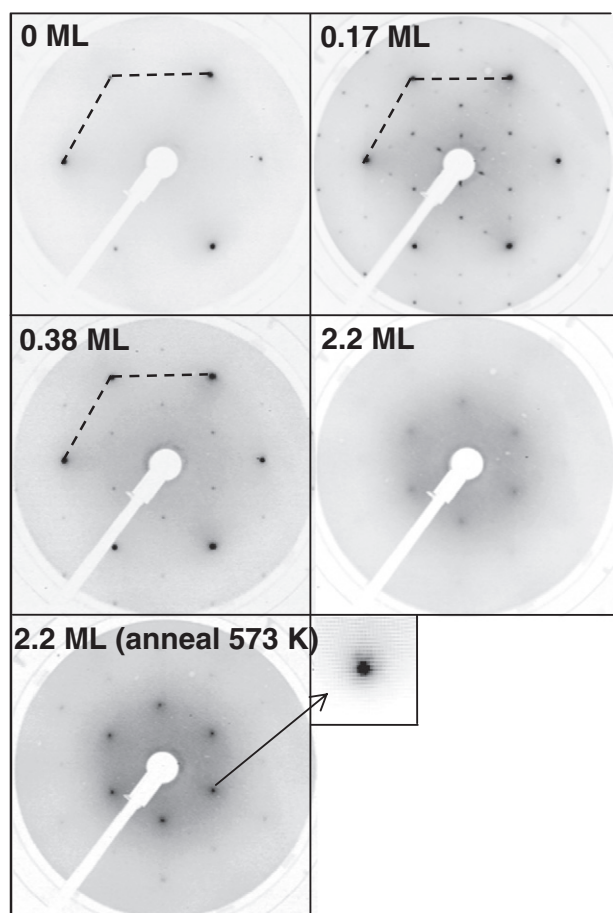

Fig. 1. LEED patterns of room temperature deposition of Te onto Cu(111), collected at 111 eV and at a sample temperature of 300 K. The dashed lines show the 1st Brillouin Zone of the Cu(111) substrate. The bottom right panel shows an expanded view of a single diffraction spot, where the contrast has been adjusted to pick out weak six-fold satellite spots.
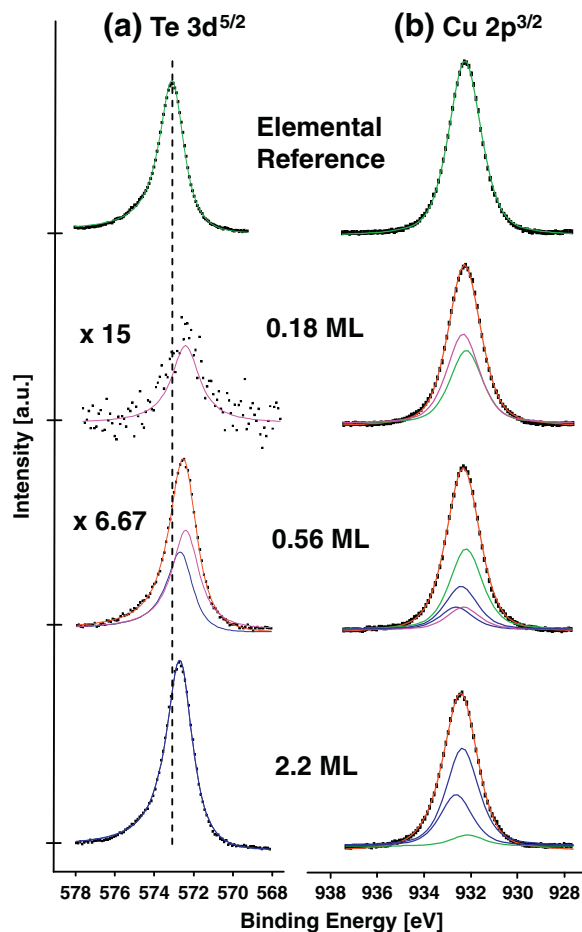

Fig. 2. XPS spectra for (a) Te 3d$^{5/2}$ and (b) Cu 2p$^{3/2}$ core levels. The upper panels show elemental (a) Te 3d$^{5/2}$ and (b) Cu 2p$^{3/2}$ reference spectra. The lower panels show Te 3d$^{5/2}$ and Cu 2p$^{3/2}$ core levels as a function of Te coverage on Cu(111). The fitted spectra are in red whilst green indicates elemental Cu or Te components; magenta represents the surface substitutional alloy (SSA) contribution and blue is the bulk alloy (BA).