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# Growth of Sn thin films on CdTe(111)

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**Abstract**

The formation and the growth of Sn films on CdTe(111) have been studied by hemispherically recorded ARXPS. The XPD patterns show that these films consist of α-Sn. XPD and ARXPS depth profile analysis reveal the presence of an intermixing zone at the interface which establishes during the initial stages of film formation.

*Keywords:* ARXPS; α-Tin; CdTe; Contact; Interface intermixing; XPD

## 1. Introduction

Thin film structures based on the semi-metal (gray) α-tin and the semiconductor CdTe have attracted considerable interest owing to their potential for device applications [1,2]. α-Sn and CdTe are almost perfectly lattice matched (0.1%) and expected to be stable in contact with each other. Most previous experimental work was carried out with substrates of (001) orientation, despite the fact that structures grown in the (111) orientation are expected to be more stable [3]. Polar interfaces between a polar and a non-polar semiconductor are of basic interest since they are predicted to reconstruct owing to built-in charge instabilities [3].

Tin exists in two modifications: white β-tin which is a metal having tetragonal structure that undergoes a phase transition at 13°C to form gray α-tin which is a semimetal having the diamond crystal structure. Although metastable at deposition temperatures of 80 to 150°C, thin crystalline films of α-Sn are stabilized by contact with a CdTe substrate.

In this study we investigated the formation of the Sn/CdTe(111) interface as well as the growth of thin Sn films on CdTe(111). The Sn layers were deposited in an UHV system and examined in situ by angle-resolved X-ray photoemission spectroscopy (ARXPS), including X-ray photoelectron diffraction (XPD) and compositional depth profile analyses in the surface region of about 50 Å thickness. A novel direct crystallographic method CHRISDA [4] (Combined Holographic Real Space Imaging by Superimposed Dimer Function Algorithm) is employed for the evaluation of the XPD. CHRISDA allows one to determine the crystal structure, to identify twins and (for very thin films) to analyze surface reconstructions.

## 2. Experimental

The samples used were Bridgeman grown CdTe(111) and $Cd_{0.96}Zn_{0.04}Te(111)$ single crystals.

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The samples were chemically etched and subsequently cleaned by a $CH_4/H_2$ based plasma process [5]. This treatment completely removes surface contamination (e.g. hydrocarbons, native oxides and amorphous tellurium) and results in a stoichiometrically composed surface which is smooth on the atomic scale. From the plasma reaction chamber the samples were transferred under ultrahigh vacuum conditions to the analysis chamber. After the plasma treatment the samples showed a clear (1 × 1) LEED pattern and well-developed (X-ray) photoelectron diffraction (XPD) patterns [6,7]. The presence of a LEED pattern at the initial substrate surface proved to be a necessary condition for obtaining single crystalline films of α-Sn. High purity Sn was evaporated from a molybdenum crucible by electron bombardment. The deposition rate was 0.5 Å/min at a base pressure of better than $p = 10^{-7}$ Pa. Film uniformity was ensured by continuous rotation of the sample, which was mounted on a heatable stage. The film thickness was measured by a flux monitor built in the evaporation gun. For additional calibration of the thickness, a quartz crystal microbalance was put in place of the sample.

## 3. Results and discussion

Providing information on the individual atomic environment of Cd, Te and Sn, XPD proved to be a very viable tool for the characterization of the crystalline structure of the deposited films. In contrast to other reports [8], we found even for the CdTe(111) surface that the deposited Sn film crystallizes in the α-phase (diamond structure). On the Cd-terminated A-face as well as on the Te-terminated B-face, the film grows in registry with the substrate (i.e. without a stacking fault). The temperature region allowing for the growth of a single-crystal layer is relatively small. At room temperature the film grew typically as a twinned layer of ⟨111⟩ oriented regions of α-Sn. Polycrystalline films of α-Sn with a random orientation or a fiber texture were obtained if the initial surface displayed no LEED pattern owing to a lack of long-range order or residual hydrocarbon contamination. While for low temperature deposition a reaction of Sn with the substrate was definitely absent, for deposition at 150°C tin was found to react with the substrate to form a film consisting of a mixture of cubic SnTe, α-Sn and CdTe. Single-crystal films of α-Sn free of twinning were obtained when the substrate temperature was held at 100°C during tin deposition.

Characterization of the crystalline Sn phase forming the deposited film was straightforward on the basis of the photoelectron diffraction patterns measured for the Sn 3d electrons. XPD patterns from a (111) face of a single crystal with zinc blende or diamond structure show a threefold rotational symmetry and six mirror planes (two-dimensional point group 3m1). Since a threefold rotational axis is absent in the tetragonal system, β-Sn could grow on the (111) surfaces only as polycrystalline material. The result of the CHRISDA analysis of the XPD pattern confirmed the diamond structure of the films. The epitaxial relationship between substrate and overlayer was established by the combined analysis of the Cd 3d, Te 3d and Sn 3d patterns obtained for thin films. Twins occurring for room temperature deposition were indicated by the simultaneous presence of regular and azimuthally-rotated lattice plane images, leading to an overall sixfold symmetry of the Sn 3d pattern. The formation of SnTe upon high temperature deposition was found by a depth profile analysis [7] of the respective ARXPS data. The presence of crystalline SnTe was indicated by CHRISDA, which showed additional lattice plane images characteristic of rock-salt.

We also investigated the initial stages of film formation. Very similar results were obtained for the CdTe(111)A and the (111)B faces as well as for $Cd_{0.96}Zn_{0.04}Te$ substrates. Fig. 1 shows the results of hemispherical ARXPS measurements performed on CdTe(111)B surfaces with nominal Sn coverages of 1 (left column), 3 (center column) and 5 ML (right column) and allows for a comparison with calculated patterns (top row). The bottom row of Fig. 1 shows compositional depth profiles which were determined by fitting modeled curves to the experimental polar-angle dependent signal fractions [7]. In Figs. 1g–1i the concentration profiles of Sn, Cd and Te are shown as shaded areas and are expressed in terms of the chemical

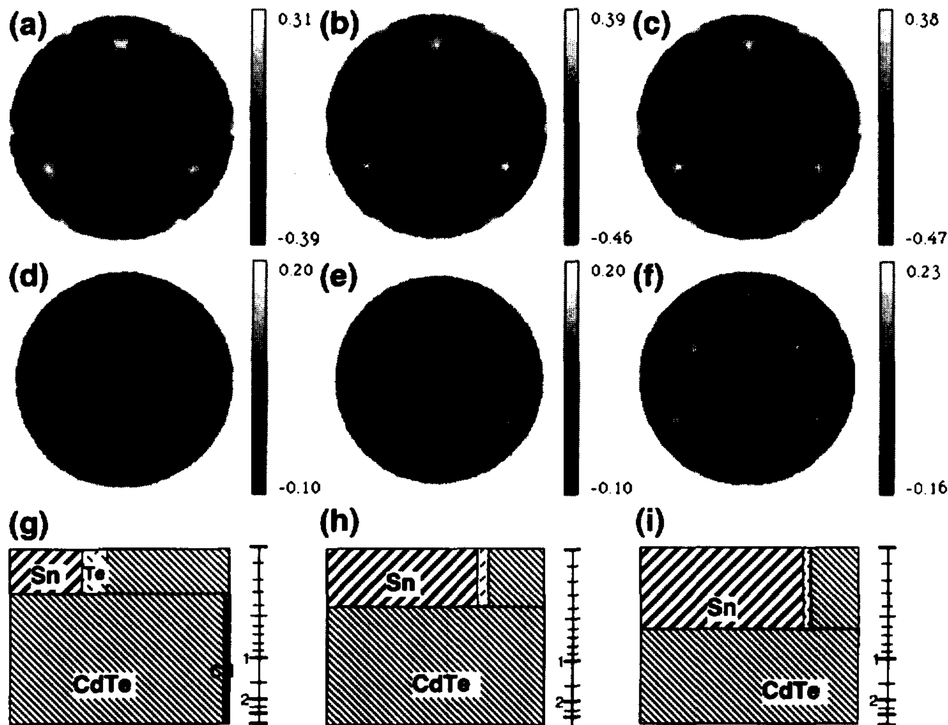


Fig. 1. Hemispherically recorded ARXPS data of the Sn3d photoelectrons for different coverages of Sn. The experimental ARXPS data have been processed to obtain polar-angle dependent average signals and normalized anisotropy contrast patterns (center row). The ARXPS depth profiles (bottom row) are derived from the polar-angle dependent signal fractions. The left, center and right columns correspond to nominal Sn coverages of 1, 3 and 5 ML. The anisotropy contrast patterns in the top row are the result of a single scattering calculation (dimer function approximation) for Sn 3d photoemission from uniform α-Sn overlayers with nominal thickness of (a) one, (b) two and (c) three bilayers. The circles indicate for the topmost bilayer plane, the direction of those scatterers which are nearest to an emitter in the bottom layer.

phases the components can be assigned to, namely Sn, (Te) and CdTe. The slight excess of Te present in these depth profiles indicates the Te termination of the substrate. The scale of the depth profiles is referred to units of the escape length of the photoelectrons. The escape length was determined by the correlation between the measured amount of deposited tin and the amount resulting upon the ARXPS depth profile analysis. Consistently, for all profiles, a value of 20 Å was obtained for the escape length of the Te 3d electrons ($E_{kin} = 676$ eV). As an important result of the depth profiles in Figs. 1g–1i it is evident that the Sn layer on the substrate does not form a closed uniform film at the early stage of film formation.

The CHRISDA analysis of the anisotropy contrast patterns in Figs. 1d–1f lead to a similar result. Sharp images of scattering planes above the emitter occurred exactly at the distances and in the stacking sequence characteristic of α-Sn. The number of detected planes increased from one (for Fig. 1d) to six (for the pattern of Fig. 1f) and is an estimate of the maximum local layer thickness if the emitter is assumed to be at the bottom of the overlayer. For a direct assessment of this thickness we calculated the Sn 3d photoemission patterns for uniform and unreconstructed α-Sn overlayers with nominal thicknesses of one, two and three bilayers (Figs. 1a–1c, respectively). As for the CHRISDA analysis the dimer function approximation was used for this calculation. Apart from the prevailing features of forward scattering at near neighbors, the

simulated patterns show Kikuchi bands as a combined diffraction effect of scatterers at a larger distance. In each pattern the additional most relevant forward scattering peaks resulting from scattering at the topmost bilayer have been marked by a circle. Both emission sites in the bilayer at the bottom have been regarded. The comparison between Figs. 1a to 1c demonstrates that with each increment of the overlayer thickness it becomes increasingly difficult to single out features of the top bilayer. The "imaging range" is limited to about three bilayers above an emitter. The calculated patterns are in adequate agreement with the experiment, though the absence of some expected details implies that there is a lower degree of order at the real surface. The diffuse ring-like structure in Figs. 1d and 1e may indicate that the surface atoms tend to be arranged in an azimuthally, almost random, manner.

In spotting by eye the relevant features suggested with the simulated patterns we can assess the number of imaged bilayers to be one, two and three for the patterns in Figs. 1d (1 ML), 1e (3 ML) and 1f (5 ML), respectively. Consistently, the respective numbers of bilayers inferred from the layer thicknesses of the ARXPS depth profiles in Figs. 1g–1i are 1.6 (for 1 ML), 2.1 (for 3 ML) and 3.5 (for 5 ML Sn coverage), respectively.

Hence, both the ARXPS depth profiles as well as the XPD patterns show that the width of the Sn-containing region is larger than the measured average thickness of deposited Sn. This result indicates the formation of an intermixing zone between the Sn overlayer and the CdTe substrate which extends over a depth range of initially one bilayer (after deposition of 1 ML Sn) to about three bilayers (after 5 ML).

For a polar interface between a polar and a non-polar material it is not unexpected that an intermixing zone establishes. Harrison et al. [9] were the first to point out that a large electric field of the order of $10^7$ V/cm would be present at an ideal interface between a polar and a non-polar semiconductor. Though a charge redistribution in the bonds will produce an additional polarization dipole in the bond it cannot remove the charge accumulation which arises from the charge sheets of the ionic cores. Hence, this field would lead to an instantaneous breakdown of the ideal interface by mixing of the polar and non-polar constituents (HKWG rearrangement [10]). The intermixed region is expected to extend over more than just a single interfacial layer [9]. If the HKGW rearrangement goes to completion, there should be no energetic preference for the orientation and termination of a growing polar semiconductor on a non-polar substrate, or, vice versa, the growth of a non-polar semiconductor on the termination of a polar substrate [10]. The predicted absence of an energetic preference for Sn deposition on the termination of the CdTe(111) substrate could well explain the similarities of our XPD results observed for the A and the B faces.

Though we favor intermixing at the interface as explanation for the data of Fig. 1, this cannot be concluded exclusively from our data. Similar ARXPS depth profiles and XPD patterns would also be expected to result if tin condensed as patchy islands of some ML height on the surface. Though we did not find direct experimental evidence disproving such an interpretation, layer growth initiated by island formation would be rather unusual for the perfectly lattice matched Sn/CdTe system. A Stranski–Krastanov growth mode of the tin film, as reported for the (110) surface [11], can be definitely ruled out for the investigated (111) surfaces, since the presence of a closed tin layer is inconsistent with the profiles of Fig. 1 and the respective ARXPS data (even if additional depth zones are introduced).

We could not determine the exact amount of tin required to form a closed film; however, upon deposition of 20 ML Sn a closed film had formed since the XPS signals for Cd and Te had decreased below the detection limit.

## 4. Summary

Using hemispherically recorded photoelectron diffraction for surface analysis we have investigated the growth of Sn films on CdTe(111) and $Cd_{0.96}Zn_{0.04}Te(111)$ substrates. The deposited Sn film crystallizes in the α-phase and grows

epitaxially on the substrate. Single-crystal films of α-Sn free of twinning were obtained when the substrate temperature was held at 100°C during tin deposition.

A new technique (CHRISDA) for the analysis of hemispheric XPD data was successfully applied to determine the crystalline structure of the Sn films and the surface structure during the initial stages of film formation. These results are compared with the ARXPS depth profiles independently obtained from the angle-averaged signal fractions.

The CHRISDA results are consistent with film growth proceeding in a bilayer-by-bilayer mode. ARXPS depth profiles and structural CHRISDA depth profiles of layers obtained after deposition of 1 to 5 ML consistently suggest that there is intermixing at the α-Sn–CdTe interface, extending at least over two bilayers. An intermixing zone is expected to establish for a polar interface of the investigated type. An intrinsic intermixing of α-Sn/CdTe interfaces is likely to have a strong impact on the electronic properties of a respective heterojunction and therefore will influence the performance of most devices based on this material system.

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