

Home Search Collections Journals About Contact us My IOPscience

CdI<sub>2</sub> single-crystal growth on Cu(111): adsorption, desorption and formation of a chemisorbed CdI<sub>1</sub> phase

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1996 J. Phys.: Condens. Matter 8 3285

(http://iopscience.iop.org/0953-8984/8/19/004)

View the table of contents for this issue, or go to the journal homepage for more

Download details: IP Address: 171.66.16.208 The article was downloaded on 13/05/2010 at 16:37

Please note that terms and conditions apply.

# $CdI_2$ single-crystal growth on Cu(111): adsorption, desorption and formation of a chemisorbed $CdI_1$ phase

Roslinda Ithnin and Robert G Jones†

Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, UK

Received 15 December 1995, in final form 16 February 1996

**Abstract.** The adsorption and desorption of CdI<sub>2</sub> on Cu(111) has been studied using Auger electron spectroscopy and low-energy electron diffraction. Multilayer adsorption occurs at room temperature via a layer-by-layer growth mechanism. The first chemisorbed layer, consisting of 1/3 ML of iodine and 1/6 ML of Cd, has a  $(\sqrt{3} \times \sqrt{3})$ R30° structure. Subsequent layers, consisting of hexagonal I···Cd···I sandwich layers, grow as single crystal with the hexagonal CdI<sub>2</sub> unit mesh vectors (4.24 Å in length in the bulk material) parallel to and coincident with the Cu(111)  $\sqrt{3}$  distance (4.42 Å in length). The ' $(\sqrt{3} \times \sqrt{3})$ R30°' diffraction beams therefore persist even for very thick layers of CdI<sub>2</sub> as they are the first-order diffraction beams of the CdI<sub>2</sub> single crystal. The CdI<sub>2</sub> multilayers desorb between 380 and 410 K, leaving a surface having the stoichiometry CdI<sub>1</sub>, consisting of 1/3 ML of iodine and 1/3 ML of Cd, which exhibits a good ( $\sqrt{3} \times \sqrt{3}$ )R30° structure in which the Cd probably lies between the iodine adlayer and the copper surface. Between 420 and 450 K, cadmium is lost from this surface, presumably by desorption, leaving a ( $\sqrt{3} \times \sqrt{3}$ )R30° structure composed of 1/3 ML of pure iodine. A structure is proposed for the CdI<sub>1</sub> adlayer and the mean free paths of the Auger electrons through the CdI<sub>2</sub> multilayer are calculated.

#### 1. Introduction

Many layered transition metal halides have a 'sandwich layer' structure consisting of two hexagonal close-packed layers of halogen ions with the metal ions in the interstices between the layers. These 'sandwich layers' have strong intralayer chemical bonding but weak van der Waals interlayer bonding. Such materials present an intriguing case when adsorbed on a surface, as the strong intralayer bonding will tend to maintain the integrity of the sandwich layer, while the bonding to the substrate will tend to disrupt it.

We have carried out two studies of such layered halides,  $CdI_2$  [1] and  $PbI_2$  [2] grown on the semiconductor InSb(001). Lead iodide, with a hexagonal unit mesh of lattice constant 4.557 Å [3], can be aligned with one side of this mesh very nearly coincident with one side of the square unit mesh of InSb(001), which has a lattice constant of 4.581 Å [3], leading to single-crystal growth of the PbI<sub>2</sub> on the InSb.

However, cadmium iodide has a smaller hexagonal mesh of lattice constant 4.24 Å, which surprisingly still leads to single-crystal growth, but with the angle between the adlayer and substrate meshes set at  $7^{\circ}$  [1]. Such behaviour, in which incompatible crystal faces grow together (square and hexagonal here), is known as rotational epitaxy [4]. The angle of rotation is related to the minimization of the interfacial energy and has been discussed in our previous papers [1, 2].

<sup>†</sup> Corresponding author.

<sup>0953-8984/96/193285+11\$19.50 (</sup>c) 1996 IOP Publishing Ltd

# 3286 R Ithnin and R G Jones

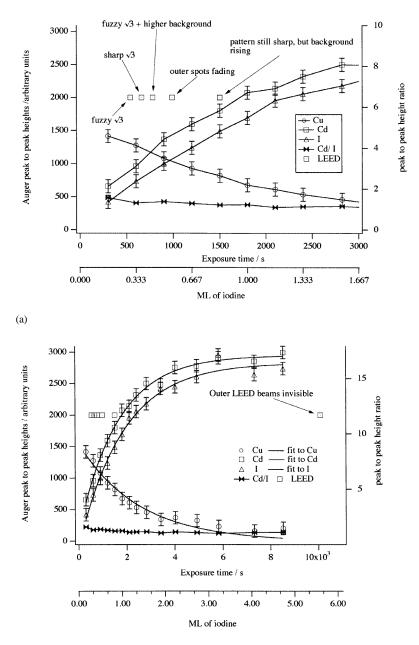
Such behaviour is of both academic and industrial interest. The pre-eminence of silicon in the semiconductor industry is due partly to its ability to form an insulating oxide layer of high integrity, on which conducting layers can be laid down, while other potentially useful semiconducting materials do not form this useful insulating oxide layer. The ability, using rotational epitaxy, to grow insulating, semiconducting and conducting single crystals one on another without the need for lattice matching has exciting consequences of obvious interest to the semiconductor industry.

The study presented here takes our initial halide (insulator) growth on InSb(001) (semiconductor) and extends it to the growth of layered halides (insulators) on metals (conductors). The metal surface chosen was Cu(111), as it is a frequently used conductor with a well understood surface chemistry which is relatively unreactive and hence less perturbing to the adlayer. As far as we are aware this is the first study of the growth of a halide on a metal under UHV conditions, though the reverse situation, the growth of ultrathin copper crystals on NaCl crystals [5], is well established.

The only study in the literature relevant to the present work concerns the electrochemical growth of CdS on Au(111) [6]. CdS is a layered material having the wurtzite structure. It was grown on the Au(111) surface by sequential deposition of Cd and S, followed by analysis using scanning tunnelling microscopy. The CdS grew epitaxially on the Au(111) with the hexagonal base of the wurtzite unit cell parallel to the Au(111) surface with the unit mesh vectors of the CdS parallel to the Au(111) unit mesh translation vectors. The CdS unit cell expanded by  $\simeq$ 4% parallel to the Au(111) surface, which allowed the CdS unit mesh to come into coincidence with the Au(111) substrate to form a (3 × 3) coincidence structure.

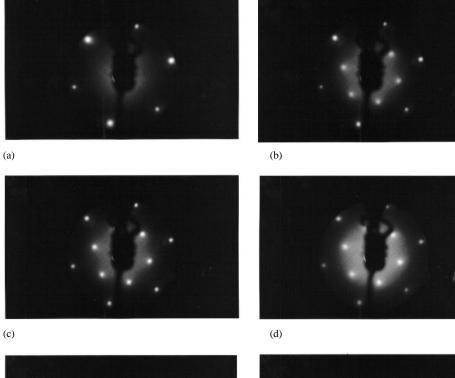
## 2. Experimental details

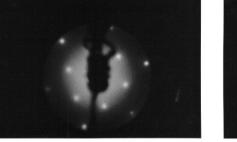
The experiments were carried out in a stainless steel ultrahigh-vacuum chamber which has already been described [1, 2]. Low-energy electron diffraction (LEED) was carried out using a 7.1  $\mu$ A beam of 2.2 mm diameter, while Auger electron spectroscopy (AES) was carried out using a defocused 2 keV, 15.6  $\mu$ A, 2.2 mm diameter beam with 3 V rms oscillation of the sample, phase-sensitive detection and data acquisition under computer control. The CdI<sub>2</sub> was produced using a solid state iodine source [7] operated at 523 K, which is above its usual operating temperature, to evaporate CdI<sub>2</sub> [1]. All exposures are given in seconds, as the flux of  $CdI_2$  at this fixed temperature was not known. The iodine source, which consisted of a 10 g pellet of AgI(95%)/CdI<sub>2</sub>(5%) (wt%) in a Pyrex tube 10 cm long by 1 cm in diameter,  $\simeq 12$  cm from the sample, was left open circuit so that no molecular iodine was produced (this was checked using a quadrupole mass spectrometer). AES scans of the sample showed no transitions due to silver, confirming that AgI has a negligible pressure at the evaporation temperature of 523 K. A simple shutter between the CdI<sub>2</sub> source and the sample allowed the  $CdI_2$  flux to be shut off from the sample. The copper sample was 10 mm in diameter by 1 mm thick. After chemical etching at 343 K in a 1:1:1 mixture of nitric acid ( $\simeq 16$  molar), orthophosphoric acid ( $\simeq 16$  molar) and glacial acetic acid for 60 s, it was mechanically polished to a mirror finish using diamond paste. In vacuo cleaning was by argon-ion bombardment, 1 keV,  $45^{\circ}$  to the surface, 4  $\mu$ A cm<sup>-2</sup>, 15 min, followed by 10 minutes of annealing between 723 and 773 K. This produced a clean surface exhibiting a sharp  $(1 \times 1)$  LEED pattern and only the copper Auger electron peaks.

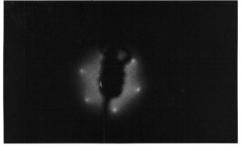


(b)

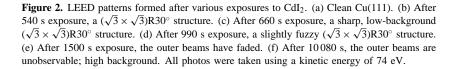
**Figure 1.** (a) Cu (911 eV), Cd (376 eV) and I (511 eV) Auger peak-to-peak heights and the  $Cd_{pp}/I_{pp}$  Auger peak-to-peak height ratio as a function of exposure time to  $CdI_2$ . Also shown are the exposure times at which particular LEED patterns were observed and a coverage scale in ML of iodine where a complete layer of iodine has a coverage of 0.33 ML (see the text). (b) As (a), but showing the data to higher exposures. Also shown are the exponential fits to the Cu, Cd and I peak to peak intensities.







(e)



(f)

### 3. Results

#### 3.1. Adsorption

CdI<sub>2</sub> was adsorbed onto the surface at normal incidence at a substrate temperature of  $308 \pm 5$  K. Three Auger electron peak-to-peak heights were monitored: the substrate Cu 911 eV peak, and the overlayer iodine 511 eV and Cd 376 eV peaks. Figure 1 shows how these Auger peak heights changed, while figure 2 shows how the LEED patterns evolved, during adsorption. A  $(\sqrt{3} \times \sqrt{3})$ R30° structure rapidly formed, becoming sharp with a low background by 660 s. Further adsorption caused some deterioration of the adsorbate-induced

spots, an increase in background and, for very large exposures,  $>10^4$  s, a complete loss of all but the innermost diffraction beams. Figure 1(b) shows how exponential curves of the form

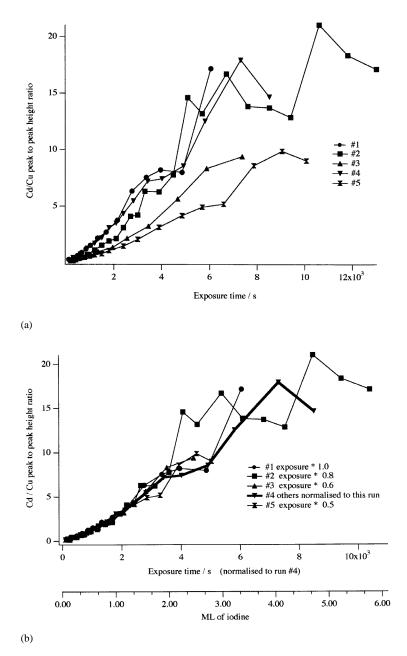
$$I = K_0 + K_1 \exp(-K_2 t)$$
 (1)

can be fitted to the AES data, where I is the peak-to-peak intensity, t is the exposure time in seconds, and  $K_0, K_1$  and  $K_2$  are constants with  $K_0 = 0$  for the copper data. The good fits of these exponentials to the experimental data show that the adsorption followed layer-on-layer growth kinetics. However, we do not think that each layer was completed prior to nucleation of the next (the Frank-van der Merwe growth mode [8]) as there were no abrupt changes in gradient visible in figures 1(a) and 1(b). We feel that it is more likely that several incomplete layers grew simultaneously [8], but without crystallite growth. This is best pictured as each layer only being completed after two or three subsequent layers have already started to grow on it. Such a growth mode leads directly to exponential increases/decreases in the Auger electron peaks, with no breaks in gradient. The cadmium Auger peak-to-peak (Cdpp) to iodine Auger peak-to-peak height (Ipp) ratio (Cdpp/Ipp) had an initial value of  $\simeq 1.4$ , which decreased slightly to  $\simeq 1.1$  after an exposure of 2000 s. The ratio then remained constant at  $\simeq 1.1$  up to exposures  $> 10^4$  s. This constant value for Cd<sub>pp</sub>/I<sub>pp</sub> confirms that the cadmium iodide was being deposited in a fixed ratio of I to Cd (which we assume to be the stoichiometric ratio of  $CdI_2$ ) throughout the adsorption. The slightly increased value during the first 2000 s suggests more complicated behaviour during the initial stages of adsorption, which will be discussed below.

The  $I_{pp}/Cu_{pp}$  and  $Cd_{pp}/Cu_{pp}$  ratios ( $Cu_{pp}$  is the copper peak-to-peak height) varied as functions of exposure time from run to run. Figure 3(a) shows representative data for  $Cd_{pp}/Cu_{pp}$ . These differences, which were attributed to variations in the  $CdI_2$  flux from one run to the next, could be eliminated by simply normalizing the exposure times to a single curve, the one used in figure 1 (by multiplying the exposures for each experiment by an arbitrary constant for that experiment). The same set of constants, when used for the  $I_{pp}/Cu_{pp}$  ratios, normalized them to a single curve also, as would be expected. Figure 3(b) shows the same data as figure 3(a) after normalizing the exposure scale in this way. Note that the increasing gradient of the curve for increasing coverage is a natural consequence of using peak-to-peak height ratios. As  $Cu_{pp} \rightarrow 0$  the ratio  $Cd_{pp}/Cu_{pp} \rightarrow \infty$ .

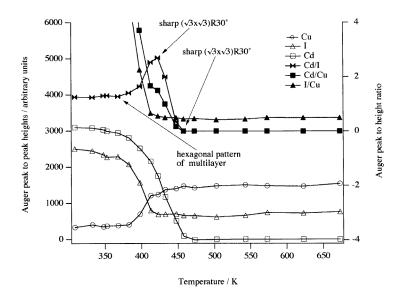
#### 3.2. Desorption

Starting with a surface formed by a normalized exposure of >6000 s of CdI<sub>2</sub>, the sample was heated to successively higher temperatures for 120 s, followed by cooling to <343 K and analysis using AES and LEED. Figure 4 shows how the copper, cadmium and iodine Auger peak-to-peak heights, and the relevant peak-to-peak height ratios, changed for these increasing annealing temperatures. A small decrease in the Cd and I peaks occurred after annealing to 380 K, but between 380 and 410 K both peaks showed a precipitate drop as the multilayers of CdI<sub>2</sub> desorbed. Close examination of figure 4 shows that the iodine and the cadmium Auger peaks did not remain proportional to each other during the latter part of this desorption process, in the temperature region of 420 K. The effect is best seen using the Cd<sub>pp</sub>/I<sub>pp</sub> ratio, also shown in figure 4. Between 300 and 380 K the Cd/I ratio had a value of  $\simeq 1.3$ , close to that found during adsorption, but between 380 and 410 K, as the multilayers desorbed, the ratio rose to 2.6, indicating a stoichiometry of CdI<sub>1</sub> at 410 K. At this point the iodine coverage had dropped to a value which remained constant even after annealing to >650 K, implying that it was a single chemisorbed layer; see below.

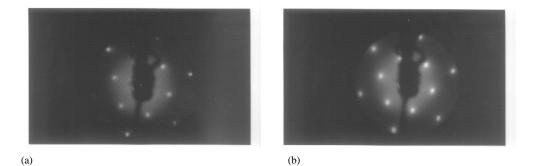


**Figure 3.** (a)  $Cd_{pp}/Cu_{pp}$  ratios for five separate adsorption runs, showing a variation in flux of  $\simeq 2$  times. (b) The same data as in (a), but with all exposure times normalized to that of experiment No 4, used in figure 1, illustrating that all the plots are of the same shape.

surface having the stoichiometry CdI<sub>1</sub> enjoyed a brief period of stability to  $\simeq$ 420 K, beyond which cadmium was lost from the surface, without loss of surface iodine, the cadmium coverage reaching zero after annealing to  $\simeq$ 450 K. After annealing to between 450 and 650 K, the surface maintained a constant iodine coverage, and exhibited a ( $\sqrt{3} \times \sqrt{3}$ )R30°



**Figure 4.** Cu (911 eV), Cd (376 eV) and I (511 eV) Auger peak-to-peak heights and Cd<sub>pp</sub>/Cu<sub>pp</sub>,  $I_{pp}/Cu_{pp}$  and Cd<sub>pp</sub>/I<sub>pp</sub> Auger peak-to-peak height ratios as a function of annealing temperature for a surface formed by a normalized exposure of >6000 s of CdI<sub>2</sub>.



**Figure 5.** LEED patterns formed after heating to (a) 423 K due to Cu(111)– $(\sqrt{3} \times \sqrt{3})R30^\circ$ –CdI<sub>1</sub> and (b) 458 K due to Cu(111)– $(\sqrt{3} \times \sqrt{3})R30^\circ$ –I. Both were taken at 74 eV.

structure on cooling to 300 K; figure 5(b).

Rather interestingly, the surface exhibiting CdI<sub>1</sub> stoichiometry after annealing at  $\simeq$ 420 K also showed a well defined ( $\sqrt{3} \times \sqrt{3}$ )R30° structure; figure 5(a). A comparison of figures 5(a) and 5(b), which were taken at the same beam energy, shows a significant difference in beam intensity, with the pure iodine  $\sqrt{3}$  structure being somewhat better formed than the CdI<sub>1</sub>  $\sqrt{3}$  structure. We thus have two ( $\sqrt{3} \times \sqrt{3}$ )R30° structures, both with the same iodine coverage, but with one, the ( $\sqrt{3} \times \sqrt{3}$ )R30°–I containing only iodine while the other ( $\sqrt{3} \times \sqrt{3}$ )R30°–CdI also has an equimolar quantity of cadmium.

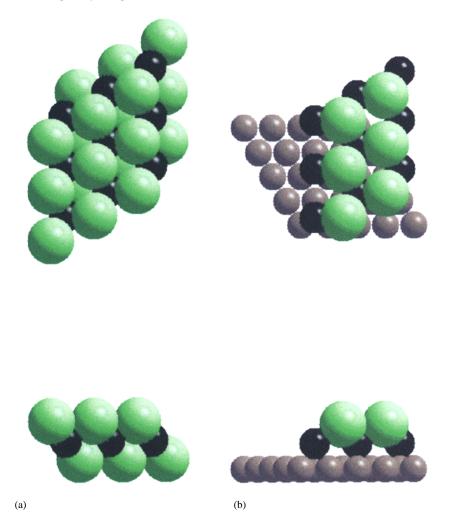
#### 4. Discussion

The I<sub>pp</sub>/Cu<sub>pp</sub> ratio for the  $(\sqrt{3} \times \sqrt{3})$ R30°–I structure formed by heating to >450 K was 0.45; figure 4. Citrin *et al* [9–11] have shown that pure iodine on Cu(111) dissociatively adsorbs to form a  $(\sqrt{3} \times \sqrt{3})$ R30°–I surface containing 0.33 ML of iodine atoms, which only begins to desorb for T > 950 K [12]. (We define 1 ML as a 1:1 ratio of adatoms to substrate surface atoms.) If we identify our pure  $(\sqrt{3} \times \sqrt{3})$ R30°–I structure formed by pure iodine on Cu(111), then the ratio I<sub>pp</sub>/Cu<sub>pp</sub> = 0.45 corresponds to a coverage of 1/3 ML, and we can calibrate the adsorption curves of figures 1 and 3(b) in ML of iodine. In figure 1(a), the sharpest  $(\sqrt{3} \times \sqrt{3})$ R30° pattern does indeed correspond to a coverage of  $\simeq 0.33$  ML.

 $CdI_2$  has a unit cell with a hexagonal base,  $a_0 = 4.24$  Å, of height 6.84 Å, containing one molecule per unit cell, while Cu(111) has a clean surface unit mesh of 2.553 Å. The  $Cu(111) - (\sqrt{3} \times \sqrt{3})R30^{\circ}$  mesh has length of side 4.42 Å, only 4% different to the hexagonal base of  $CdI_2$ . It is therefore clear that  $CdI_2$  can grow on Cu(111) with very little strain, provided that the hexagonal base is rotated by 30° with respect to the Cu(111) substrate so that its unit mesh coincides with the  $(\sqrt{3} \times \sqrt{3})$  structure of the Cu(111). The LEED patterns observed during adsorption, figures 1 and 2, are now readily explained. After 0.33 ML of iodine (0.16 ML of Cd) have been adsorbed a sharp ( $\sqrt{3} \times \sqrt{3}$ )R30° structure was observed, caused by a single layer of iodine atoms with the cadmium atoms in some as yet unspecified positions either above the iodine, co-planar with it, or between the iodine layer and the copper surface. Further adsorption to 0.66 ML of iodine (0.33 ML of Cd) would then be sufficient for a complete sandwich layer of CdI<sub>2</sub> to form, consisting of two layers of iodine atoms with cadmium in the interstices between them. This structure would also give a  $(\sqrt{3} \times \sqrt{3})$ R30° structure, but we think it unlikely that this structure was formed; see below. Subsequent adsorption to higher coverages then formed multilayers of  $CdI_2$  in which, we assume, the structure was the same as for bulk  $CdI_2$  with  $I \cdots Cd \cdots I$  sandwich layers held together by relatively weak van der Waals forces. The nonintegral-order beams in the  $(\sqrt{3} \times \sqrt{3})$ R30° diffraction pattern did not measurably change in position for this thick adlayer of single-crystal CdI<sub>2</sub>, because the first-order diffraction beams from the CdI<sub>2</sub> single crystal lie in almost identical positions. However, it was noticeable for the thicker adlayer, where the copper Auger peak had become vanishingly small, that the background in the LEED pattern did increase, due either to imperfections in the CdI<sub>2</sub> structure or possibly a lower Debye temperature, and that for very thick layers only the beams immediately adjacent to the (0, 0) beam remained visible. However, even for the thickest adlayers the diffracted beams were still quite sharp, indicating large domains of well ordered single-crystal CdI<sub>2</sub>.

Multilayer desorption of  $CdI_2$  occurred between 380 and 410 K, leaving a surface of stoichiometry  $CdI_1$ , consisting of 0.33 ML of iodine and 0.33 ML of cadmium. This surface then decomposed by desorbing cadmium and it can be seen from figure 4 that as the Cd coverage dropped to zero the copper Auger peak rose slightly, but the iodine Auger peak remained constant. This is consistent with the cadmium atoms lying between the iodine layer and the copper substrate. At no point could a stable surface be identified which consisted of a single sandwich layer of the stoichiometric  $CdI_2$ , i.e. a complete  $I \cdots Cd \cdots I$  sandwich on the clean Cu(111) surface. It follows that even a relatively inactive surface such as Cu(111) is capable of strongly perturbing the chemisorbed layer of cadmium iodide to such an extent that the stoichiometry is altered.

Citrin *et al* [9–11] have shown using SEXAFS that the iodine in Cu(111)– $(\sqrt{3} \times \sqrt{3})$ R30°–I resides in the threefold coordinate hollows. If we take this structure and insert 0.33 ML of Cd between the copper surface and the iodine layer, we can generate a possible



**Figure 6.** (a) The plan and elevation of one sandwich layer of the bulk CdI<sub>2</sub> structure. The larger lighter atoms are the iodine atoms, the smaller, darker atoms are the Cd ions in the octahedral holes between the two iodine layers.  $a_0 = 4.24$  Å,  $c_0 = 6.84$  Å. (b) The plan and side elevation of a possible structure for Cu(111)– $(\sqrt{3} \times \sqrt{3})$ R30°–CdI<sub>1</sub>. The iodine (large pale atoms) and Cd (small dark atoms) are in threefold hollow sites of the copper surface (small pale atoms). All atoms are shown with their hard-sphere metallic radius ( $r_{Cu} = 1.278$  Å,  $r_{Cd} = 1.489$  Å) or van der Waals radius ( $r_{I} = 2.20$  Å). The Cd is 2.34 Å above the plane of the Cu atoms which gives a Cu···Cd distance of 2.767 Å (=1.278 + 1.489) equal to the sum of the metallic radii. The I is located 4.04 Å above the Cu plane, i.e. 1.7 Å above the Cd plane, the same distance as for bulk CdI<sub>2</sub>. Note that the stoichiometry is CdI<sub>1</sub>, whereas the stoichiometry of the bulk compound is CdI<sub>2</sub>.

hard-sphere model of the Cu(111)– $(\sqrt{3} \times \sqrt{3})$ R30°–CdI<sub>1</sub> surface; figure 6. The cadmium atoms have been arbitrarily placed in threefold hollow sites, at a height of 2.34 Å determined by the hard-sphere metallic radii of cadmium,  $r_{Cd} = 1.489$  Å, and copper,  $r_{Cu} = 1.278$  Å. The iodine layer has been shifted to 1.7 Å higher than the cadmium, which is the separation found in bulk CdI<sub>2</sub>. This has the effect of placing the iodine layer 4.04 Å above the copper layer, much greater than the 2.25 Å height calculated using the Cu–I bond distance of 2.69 Å and threefold hollow site [9–11] for the pure Cu(111)– $(\sqrt{3} \times \sqrt{3})$ R30°–I surface.

As the desorption temperature is only  $\simeq 130$  K higher than the adsorption temperature, we might assume that any rearrangement processes operative in forming the Cu(111)–  $(\sqrt{3} \times \sqrt{3})$ R30°–CdI<sub>1</sub> surface during desorption may also be operative during adsorption at  $\simeq 300$  K. If this is the case, then initially a Cu(111)– $(\sqrt{3} \times \sqrt{3})$ R30°– $\frac{1}{2}$ (CdI<sub>2</sub>) surface is formed consisting of a single layer (0.33 ML) of iodine atoms in a  $(\sqrt{3} \times \sqrt{3})$ R30° arrangement with only 0.16 ML of Cd adsorbed randomly in the threefold hollows below the iodine layer. If the cadmium were ordered, then the lower coverage of 0.16 ML would require a unit mesh larger than the  $(\sqrt{3} \times \sqrt{3})$ R30°. As no other LEED patterns were observed, we assume that the cadmium was randomly distributed. Further adsorption probably then leads directly to multilayer formation of I ··· Cd ··· I sandwich layers on this initial chemisorbed layer. However, the adsorption curves in figure 1 show that the Cd<sub>pp</sub>/I<sub>pp</sub> ratio starts at a slightly elevated value and then drops as the first three layers (1 ML) of iodine are formed. This could be due to partial formation of the CdI<sub>1</sub> surface at the CdI<sub>2</sub>– Cu(111) interface, in which there is an enhancement of the Cd concentration and loss of iodine concentration.

Irrespective of whether the  $CdI_1$  phase is formed during adsorption, or only during desorption, there is the problem of what happens to the iodine liberated in the reaction

$$\operatorname{CdI}_2 \to \operatorname{CdI}_1 + \mathrm{I}.$$
 (2)

It is just possible that atomic iodine could desorb from the surface, as the Cd–I bond strength of 138 kJ mol<sup>-1</sup> would give a rate of desorption of  $\simeq 10^{-3}$  of a monolayer per second, which is compatible with the time our experiments took. We were unable to monitor emission into the gas phase in our experiments and so we could not test this idea. A more likely possibility is that the iodine atoms diffuse to the copper surface and react, possibly at defect sites, to form crystallites of CuI (the Cu–I bond energy is 197 kJ mol<sup>-1</sup>). Such corrosion reactions have been observed [13] for Cu(111) after large exposures to I<sub>2</sub>. The crystallites, being three dimensional, would contribute only a small iodine Auger signal, thus explaining why the iodine lost in the above reaction seems to be invisible to AES.

The  $CdI_1$  phase was destroyed by heating to >450 K by loss of cadmium, but without any apparent loss of surface iodine. This can be explained if the following reaction occurs:

$$CdI_{1 ads} \rightarrow I_{chem} + Cd_{ads}.$$
 (3)

The iodine layer moves closer to the Cu(111) surface to form a strong chemisorption bond, and in so doing can be thought of as squeezing the cadmium out from between the copper surface and the iodine layer and onto the top of the chemisorbed iodine layer. Elemental cadmium has a vapour pressure of  $\simeq 10^{-5}$  mbar at 450 K [14], so desorption of cadmium atoms once they have moved to the top of the iodine layer, is prompt. The driving force for this reaction is the formation of the strong Cu–I chemisorption bond, which cannot be fully formed when the cadmium atoms reside between the iodine adlayer and the copper surface.

The mean free paths for the Cd (376 eV), I (511 eV) and Cu (911 eV) Auger electrons through the CdI<sub>2</sub> multilayer can be calculated from the fits shown in figure 1(a) by assuming that each exposure of 1200 s deposits a layer one bulk CdI<sub>2</sub> unit cell thick, 6.84 Å [3], comprising two complete layers of iodine (2/3 ML) with the stoichiometric quantity of Cd (1/3 ML) in the interstices (we ignore any errors due to nonstoichiometry of the first chemisorbed layer here). This procedure converts the exposure time-scale to a layer thickness in Å, thus allowing the mean free paths to be determined from the least-squares fit of equation (1) to the data. The mean free paths so obtained are  $\lambda_{Cd}$  (376 eV) = 3.2 Å,

 $\lambda_{\rm I}$  (511 eV) = 3.6 Å and  $\lambda_{\rm Cu}$  (911 eV) = 4.7 Å. The errors in these numbers are about 20–30%, due to inaccuracies in the estimate for the exposure necessary to form a complete sandwich layer of CdI<sub>2</sub>. The mean free path values of  $\lambda_{\rm Cd}$  (376 eV) = 3.2 Å and  $\lambda_{\rm I}$  (511 eV) = 3.6 Å for electrons passing through CdI<sub>2</sub> on Cu(111) are significantly lower than the values,  $\lambda_{\rm Cd}$  (376 eV) = 6.9 Å,  $\lambda_{\rm In}$  (404 eV) = 9.4 Å,  $\lambda_{\rm Sb}$  (454 eV) = 11.52 Å and  $\lambda_{\rm I}$  (511 eV) = 8.6 Å for electrons passing through the multilayer growth of CdI<sub>2</sub> on InSb(001) [1], which have a similar error of 20–30% for the same reasons. The differences are bigger than the experimental errors, and seem to be real. For both systems, CdI<sub>2</sub>/Cu(111) and CdI<sub>2</sub>/InSb(001), we used 2 keV incident electron beams at approximately normal incidence with AES analysis using an angle-integrating RFA, and the growth of CdI<sub>2</sub> in both systems fitted an exponential curve rather well. We do not understand why this apparently significant difference exists.

#### Acknowledgment

RI would like to thank the University of Malaya for the award of a studentship.

#### References

- [1] Mowbray A P and Jones R G 1991 Appl. Surf. Sci. 48, 49 27; 1992 J. Phys.: Condens. Matter 4 7947
- [2] Davis A A and Jones R G 1994 Surf. Sci. 310 73
- [3] Wyckoff R W G 1963 Crystal Structures vol 1 (New York: Wiley)
- [4] Dahmen U 1982 Acta Metall. 30 63
- Ramirez R, Rahman A and Schuller I K 1984 Phys. Rev. B 30 6208
- [5] Ino S, Watanabe D and Ogawa S 1964 J. Phys. Soc. Japan 19 881
- [6] Demir U and Shannon C 1994 Langmuir 10 2794
- [7] Mowbray A and Jones R G 1989 J. Vac. Sci. Technol. A 7 3373
- [8] Argile C and Rhead G E 1989 Surf. Sci. Rep. 10 277
- [9] Citrin P H, Eisenberger P, Hewitt R C and Farrell H H 1978 J. Vac. Sci. Technol. 16 537
- [10] Citrin P H, Eisenberger P and Hewitt R C 1980 Phys. Rev. Lett. 45 1948
- [11] Citrin P H, Eisenberger P and Hewitt R C 1979 Surf. Sci. 89 28
- [12] Chiang C M, Wentzlaff T H and Bent B E 1992 J. Phys. Chem. 96 1836
- [13] DiCenzo S B, Wertheim G K and Buchanan D N E 1982 Appl. Phys. Lett. 40 888
- [14] Nesmeyanov A N 1963 Vapour Pressure of the Chemical Elements (Amsterdam: Elsevier)