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Au/InSe Schottky barrier height determination

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Résumé. — Nous avons étudié la formation de l'interface Au/InSe et mesuré une barrière de Schottky microscopique de 0,7 eV en accord avec la valeur obtenue par des mesures $I(V)$ et de photovoltage. Cette barrière est formée dès la monocouche avant toute détection de réaction chimique ou interdiffusion. Sa valeur n'est pas déterminée par le travail de sortie du métal comme supposé avec des métaux non réactifs (comportement de type Schottky) mais pourrait dépendre des premières interactions interfaciales.

Abstract. — Au/InSe interface formation was studied and a microscopic Schottky barrier of 0.7 eV was measured in accordance with the value obtained by $I(V)$ and photovoltage measurements. This barrier is formed for submonolayer coverage before any chemical reaction or interdiffusion is evidenced. Its value is not determined by the metal work function as is the case with non reactive metals (Schottky behavior) but may depend on initial interfacial interactions.

1. Introduction.

The Schottky barrier formation is very interesting to study in the case of layer compounds, some of them like MoS_2 being a prototype for the applicability of the Schottky model [1]. For other compounds like GaSe one can pass from Schottky to Bardeen behavior depending on the metal reactivity [2]. Moreover InSe is a good candidate for Schottky barrier solar cells applications [3-4].

We attempt here to test the Schottky model for Au/InSe: sense of the charge transfer, and value of the barrier height.

The macroscopic value of the Schottky barrier determined from current-voltage and photovoltage measurements is compared to the microscopic value obtained from band bending.

2. Results.

2.1 PHOTOEMISSION. — We give in figure 1 the evolution of the valence bands of InSe with the deposited Au thickness θ in Å. A monolayer ($m.l.$) of gold is 2.36 Å (111 face) which corre-

sponds to $1.4 \times 10^{15} \text{ atoms/cm}^2$ while the InSe surface has $6.9 \times 10^{14} \text{ atoms/cm}^2$ (the $m.l.$ referred to the InSe surface is 1.16 Å). Measurements were made with He I radiation (21.2 eV) and at normal analysis with an angular resolved spectrometer [5]. The samples were peeled *in situ* in ultra-high vacuum (10^{-10} mb range) and the surface cristallography was checked by low energy electron diffraction. Gold was evaporated from a tungsten wire (the sample being at room temperature) and the deposited thickness was measured with a quartz microbalance. The InSe sample is intrinsic (not intentionally doped) and it has been shown that there is no band bending at the layer compounds surface [6].

Features ABCD at $\theta = 0$ are characteristic of the InSe valence bands: A is due to In and Se p_z orbitals of the In-In bond, B is due to the $p_x p_y$ orbitals of the In-Se bond while C and D arise mainly from the antibonding and bonding s states of the In-In bond [7]. The valence bands shift upwards by 0.3 eV at sub-monolayer coverage. The Fermi level is determined from higher metallic coverages and the top of the valence bands from the cut-off of

Fig. 1. — Evolution of the InSe valence bands under deposited Au thickness θ in Å with a 21.2 eV photon energy.

the energetic distribution of the photoelectrons. So from the gap value of 1.3 eV [8] a 0.7 eV microscopic barrier is deduced. From this results we can establish the electronic scheme of the interface (Fig. 4) which shows the existence of a depletion region (positive charge space) created by electronic charge transfer from InSe to Au or to Au induced gap states and establishes a rectifying contact. The vacuum level is

Fig. 2. — Upwards band bending (●●●) and movement of the In $4d^{5/2}$ state (○○○) towards E_F as a function of Au coverage (after Ref. [5]).

Fig. 3. — Evolution of the secondary electrons cut-off under coverage θ .

obtained from the work function as determined by photoemission (the value of the ionisation energy is equal to the radiation energy minus the width of the energetic distribution of the photoelectrons from the low energy cut-off to the top of the valence bands). The low energy cut-off of this distribution is shown in figure 3 and corresponds to the onset of secondary electrons. The space charge region on the semiconductor side extends over hundreds of Å and is rapidly formed for sub-m. ℓ coverage, the vacuum level follows the band bending (dashed line in Fig. 4). On the left side in figure 4 the variation of work function under metal coverage is represented : it slightly increases for sub-monolayer coverages at half the value expected from band bending, this can be attributed to dipolar interactions, then slowly decreases due to the Stranski-Krastanov growth mode [4] until it reaches the Au work function value.

From this scheme it is clear that experimental values of the work function and of the electronic

Fig. 4. — Electronic scheme of the interface as deduced from the photoemission experiments.

affinity don't verify the Schottky relation $\varphi_B = \varphi_m - \chi_{S.C}$ which predict here charge transfer as seen before from the lower work function region $\phi_{Au} = 4.85$ eV to the higher one (ϕ InSe = 5.2 eV) in contradiction to what is observed since the band bending arises from InSe to Au charge transfer as seen before. To overcome these difficulties, one can think to introduce an « effective » work function or dipolar effects, so as to satisfy the formula, but this don't give microscopic information.

We can attempt to extract this information from careful examination of the valence bands evolution. The barrier is formed before any detectable chemical interaction while an induced density of states appears in the InSe gap. Following the barrier formation we have evidenced some interaction in the valence bands region better seen in the second derivative curves of reference 5 as a splitting of the Se p_z structure (*peak A*) which can be interpreted as interaction between Se p_z states and Au s-p states and can be associated of the In 4d behavior noted in reference 5, where the In 4d binding energy under coverage follows the band bending and has a further displacement attributed to a limited In interdiffusion (Fig. 2).

2.2 CURRENT-VOLTAGE [$I(V)$] CHARACTERISTICS. — These characteristics have been measured using the diode as obtained after the Au deposition realized during the photoemission measurements. The InSe sample has been thinned peeling its

Fig. 5. — Forward and reverse $I(V)$ characteristics for a 55 μ thick Au/InSe diode.

backside on which a non rectifying contact has been performed by Sb evaporation [9]. The characteristics obtained for a 55 μ thick diode is shown in figure 5 for forward and reverse bias on the same scale.

The Schottky barrier values φ_B can be obtained from $I(V)$ characteristics provided that a model for the electronic transport is chosen. The one based on the thermo-ionic emission is more adequate [10]. In this case, the electronic current density J is given as a function of the applied voltage V by $J = J_s \left(\exp \frac{V}{nkT} - 1 \right)$ where n is the ideality factor and

$$J_s = A^{**} T^2 \exp - \frac{\varphi_B}{nkT}$$

where $A^{**} = 120 m^*/m \text{ A/cm}^{-2}/\text{K}^{-2}$ is the Richardson Dushman constant. For the InSe case m is obtained from the components $m_{||}^* = 0.81 m_0$, $m_{\perp}^* = 0.13 m_0$ of the effective mass tensor $m^* = (m_{||}^* m_{\perp}^*)^{1/3}$ [11]. From the J_s value of 10^{-5} A/cm^2 values of the Schottky barrier ranging from 0.7 to 0.75 eV are deduced with ideality factors of 1.03 and 1.1 respectively. To analyse the forward characteristic, the serie resistance of the diode must be substracted. For layer compounds the resistivity along a direction normal to the layers is $\rho_{\perp} \sim 10^4 \Omega \cdot \text{cm}$, this high value prevents to extract with precision the ideality factor in this case as

thickness and resistivity are not known with sufficient precision. However the determination from J_s is sufficient for our purpose.

2.3 PHOTOVOLTAIC EFFECT OF Au/InSe CONTACT.

— Photoelectric measurement is an accurate and direct method of determining the barrier height. If the photocurrent per absorbed photon, in the spectral region $h\omega \geq \varphi_B$, is given by the Fowler theory : in a square root plot of the photoresponse as a function of photon energy, the extrapolated value of the linear plot should give the barrier height [10]. Such a plot is given on figure 6, for measurements performed at liquid helium temperature. Although the linear region is rather narrow it indicates a clear cut-off at 0.75 eV in good accordance with $I(V)$ measurements.

Fig. 6. — Determination of the barrier height from the cut-off of the photoelectric response.

The Au/InSe diode can be used as a photovoltaic cell with an optimum Au thickness of 100 Å to transmit the light (*front illumination*).

The spectral response of three diodes of different thicknesses is given on figure 7. The onset at 1.3 eV corresponds to the InSe gap. These spectra are in accordance to photovoltaic measurements exten-

Fig. 7. — Photovoltaic response of 3 Au/InSe diodes of different thicknesses in front illumination.

sively performed on InSe Schottky diodes in view to improve the solar efficiency [3]. The different spectral responses were attributed to thickness effects through the $[\exp - d/L - \exp - \alpha d]$ term where d is the thickness, L the diffusion length of carriers and α the absorption coefficient [4].

In conclusion the macroscopic Schottky barrier determination with two different methods allows us to take with confidence the microscopic determination of Schottky barrier from valence band bending and justify the search for a microscopic origin to the barrier height. Our results show that the barrier is already formed when chemical reactions appear : splitting of Se p_z state and In 4d shift which indicate disruption of the InSe surface and In outdiffusion. During the barrier formation an induced density of states in the gap is the only salient feature. Although the exact microscopic origin of the barrier is not clear it appears from our results that it involves the first adatom-substrate interactions.

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