Heterojunction by Photoelectrochemical Surface Transformation: n:$CuInSe_2$/p-$CuISe_3Se^\circ$

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Heterojunction formation by photoelectrochemical alteration of semiconductor surfaces is reported. Growth of a new semiconducting phase at the n-$CuInSe_2/I^-$-I_2-Cu^+ interface is achieved by controlling electrochemical parameters. The interfacial layer is identified as $CuISe_3Se^o$ and exhibits p-type conductivity. Under Illumination the interphase mediates efficient charge transfer between $CuInSe_2$ and the I^-/I_2 redox couple while inhibiting semiconductor dissolution.

Current interest in $CuInSe_2$ systems from its exceptional optoelectronic properties, resulting in the devolopment of efficient solid state (1) and photoelectrochemical (2) solar cells. Performance of the latter pivots on the growth of an interfacial layer induced by specific electrolyte composition, resulting in a substrate-film-electrolyte structure. In this note we explore the location of the photoactive junction and the circumstances leading to the $CuInSe_2$ surface transformation.

Interfacial films were grown on back ohmic contacted, epoxy insulated and etched (112) faces of n-$CuInSe_2$ by operation as photoanodes in an electrolyte consisting of 1 M I^-,0.05 M I_2, 0.02 M CuI and 2 M HI. This involved, cyclic polarization of the electrode between the potential limits of short circuit and open circuit or leaving it at the maximum power point. Film quality was monitored by the photocurrent-voltage output. Generally 3 - 4 intermediary etches were required to optimize the film performance.

Scanning electron micrographs of the electrochemically treated $CuInSe_2$ electrodes show that a polycrystalline film consisting of randomly oriented, flat, hexagonal crystallites is grown on the $CuInSe_2$ substrate (3). Crystallite sizes range between 2 - 5 microns. A cross-section of a cleaved electrode evidences that the film does not penetrate deeper than 2 microns into the substrate even after prolonged o eration (5 weeks) in a solar cell, but appears to completely cover the substrate growing into micros pic cavities.

key words: Semiconductor Interfaces, Solar Energy, Photoelectrochemistry

The distinct crystallite geometry suggests that a chemically well efined compound is grown at the $CuInSe_2$/electrolyte interface. X-ray diffraction analysis of the crystallites identifies the new phase as consisting of mainly $CuISe_3$ and up to 30 % elemental Se. No evidence for formation of polycrystalline CuI was found.

Chemical reactions of illuminated $CuInSe_2$ with the electrolyte constituents obviously transform the semiconductor surface to generate the $CuISe_3$-Se^o phase. In the absence of Cu^+ in the electrolyte, elemental Se^o and triangular crystallites of CuI have been detected on photocorroded $CuInSe_2$ surfaces (3). CuI is partly soluble in iodide solution forming CuI_2^-. Addition of Cu^+ to the solution probably raises the surface concentration of CuI_2^- to a critical value required to initiate $CuISe_3$ film growth. $CuISe_3$ crystals have been previously prepared by reacting stoichiometric mixtures of CuI and Se in HI medium under hydrothermal conditions (4). The reactants employed in the hydrothermal synthesis of $CuISe_3$ are thus provided by the electrolyte and the semiconductor components in our cell while the reaction enthalpy is probably supplied by the photopotential.

Fig. 1 compares UPS energy distribution curves, N(E) of the untreated $CuInSe_2$ single crystal and the $CuInSe_2$-$CuISe_3$-Se^o structure, with the Fermi levels E_F aligned to the edges of the valence band. E_V^n and E_V^p for the two samples differ by 0.65 eV. $|E_V-E_F|$ is 0.85 eV for $CuInSe_2$ and 0.2 eV for the film. With a bandgap, E_g^p of 2 eV for $CuISe_3$ (5) and for Se (6), the film is thus a p-type semiconductor. Measurement of the relative work functions, ϕ, of the two samples with the vacuum levels aligned also indicate that the E_F's differ by 0.65 V. Hence $E_V^n(CuInSe_2)=E_V^p(\text{film})$. Adding the electron affinity, χ^n of 4.58 eV (7) to the E_g^n of 1 eV for $CuInSe_3$ the absolute value of E_V^p is estimated to be 5.58 eV.

The energetics of the structure are given in Fig. 2. Experimental and literature values for various electronic parameters indicated with superscripts n and p refer to n-$CuInSe_2$ and p-$CuISe_3$-Se^o, respectively. An estimate for the work function of the I^--I_2-Cu^+-HI electrolyte of ϕ^e=5.1 eV is obtained by adding the measured redox potential of +0.2 V (SCE) to the more recent value of (NHE)=4.7 eV (8). Comparison of E_F^n, E_F^p and ϕ^e yields a potential of at least 0.65 eV at the substrate/film junction and of 0.2 eV($\Delta\phi$) at the film/electrolyte interface. This implies a p-n junction between the solids and a rectifying junction at the electrolyte contact. The spectral response and the anodic photocurrent, however, attest the light absorption and photogeneration of h^+ in the n-$CuInSe_2$ (2,3). A barrier at the film/electrolyte interface would impede h^+ transfer to I^-. The high quantum efficiency and the photovoltage of 0.42 V (2) argue against such a barrier and suggest that the principal potential drop occurs in the p-n junction with the electrolyte providing an ohmic contact. Interactions between the semiconductor and electrolyte upon immersion may account for the energetic difference,$\Delta\phi$,as the scheme in Fig. 2 disregards the effects of pH and specific adsorption.

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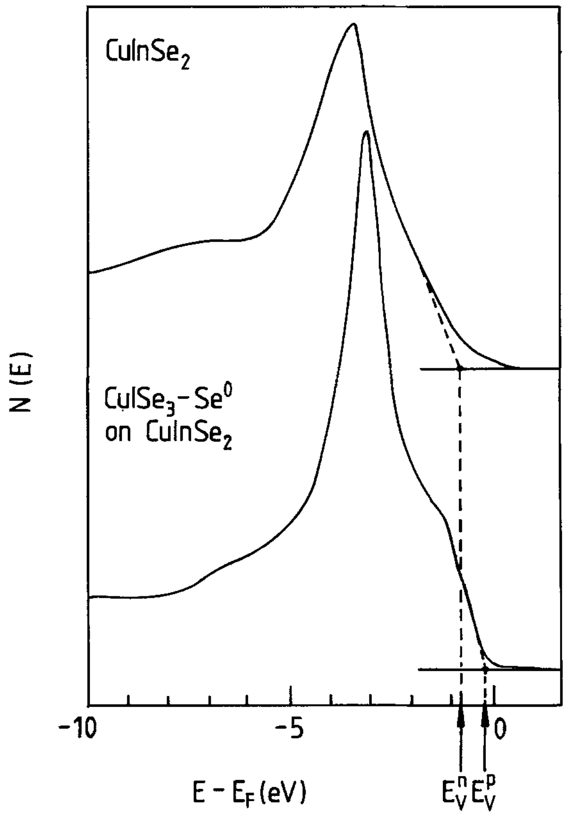

Fig.1 Energy distributions N(E) obtained by UPS using He(II) excitation ($h\nu$ = 41.8 eV).

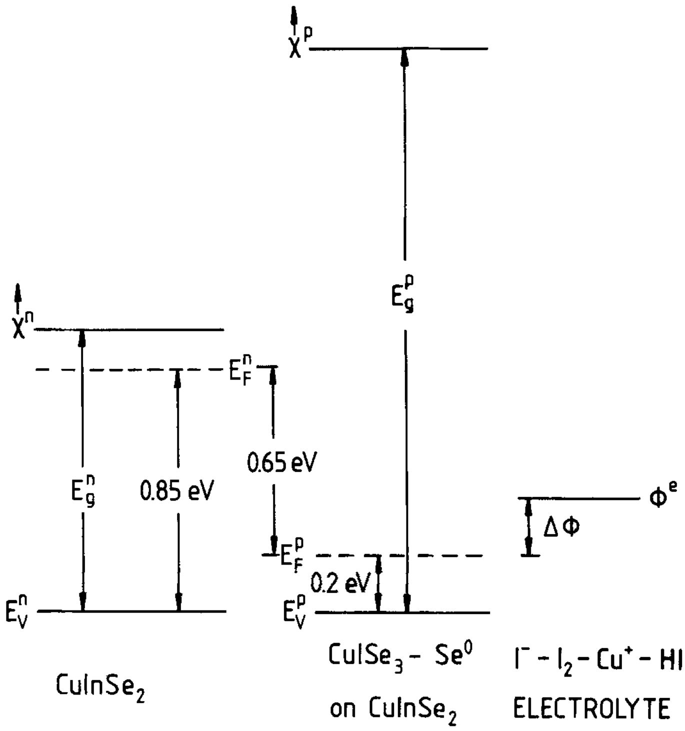

Fig.2 Schematic of energy levels of n-$CuInSe_2$, p-$CuISe_3$ and redox electrolyte.