Electrochemical Growth of a Cu_2O/PbS Epitaxial Heterojunction on Single Crystal Au(100)

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Semiconductor heterojunctions are ideal for light-harvesting devices such as photovoltaic[1,2] and photoelectrochemical[3] cells, since multiple-semiconductor devices can absorb a larger fraction of the solar spectrum than single-semiconductor devices. Epitaxial heterojunctions are desired for these applications since the transport of photogenerated electrons or holes across the interface is more efficient. In addition, multilayered semiconductor heterojunctions show quantum confinement effects in the small band-gap semiconductor when the layer thicknesses are in the nanometer range.[4] It is often possible to electrodeposit multilayered architectures from a single plating bath by simply pulsing the applied potential during growth.[5−11] The low processing temperatures (often room temperature) of electrodeposition should lead to abrupt interfaces in epitaxial heterojunctions, because interdiffusion will be minimized.

Lincot and co-workers have used electrodeposition to prepare epitaxial films of CdTe on InP[12] and ZnO on GaN.[13] Our emphasis has been on the electrodeposition of epitaxial structures with a large lattice mismatch. We have recently shown that epitaxial films of individual semiconductors such as Bi_2O_3,[14] Cu_2O,[15] and PbS[16] can be electrodeposited onto single-crystal Au.

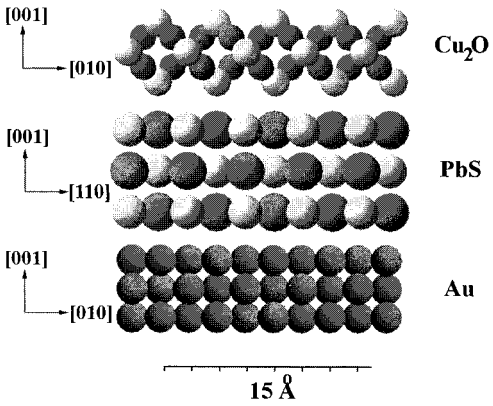

Figure 1. Schematic of the Cu_2O/PbS/Au (100) epitaxial heterojunction. Only one-unit-cell-thick layers are shown for PbS and Cu_2O, although the real thickness of the films is about 0.5 μm. The actual thickness of the Au substrate is 1 mm. The metal atoms are dark, and the nonmetals atoms are light. The arrows to the left of each structure show the crystallographic directions for each layer.

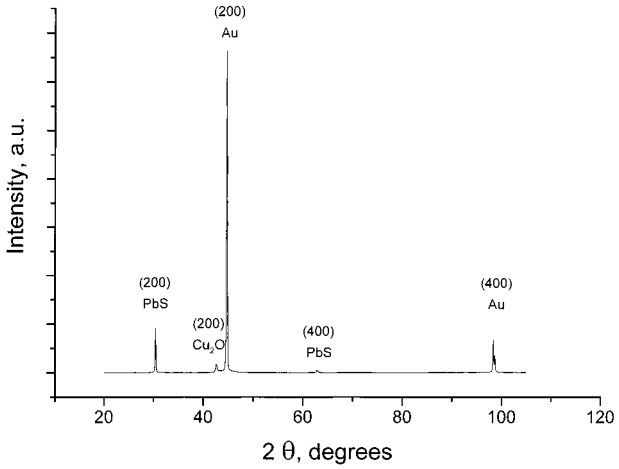

Figure 2. X-ray diffraction pattern probing the out-of-plane orientation of a heterostructure consisting of 0.5-μm-thick PbS and Cu_2O films sequentially electrodeposited onto single-crystal Au(100). Rocking curves for the (200) reflections of Au, PbS, and Cu_2O have fwhm of 0.6°, 1.1°, and 2.3°, respectively.

The large mismatch in the Bi_2O_3/Au (35.3%) and PbS/Au (45.5%) epitaxial systems was accommodated by the formation of coincidence lattices, in which the film was rotated relative to the Au substrate. The mismatch in the Cu_2O/Au system was only 4.4%, and no rotation of the film was observed. In the present paper we report the epitaxial electrodeposition of a Cu_2O/PbS heterojunction on single-crystal Au(100) (see Figure 1).

Both PbS and Cu_2O are p-type semiconductors. PbS is a low band-gap (0.4 eV) semiconductor with a face centered cubic (fcc) structure (space group $Fm3m$ and lattice parameter $a = 0.5933$ nm). Cu_2O has a larger band gap of 2.0 eV and adopts a primitive cubic structure ($Pn3m$, $a = 0.4270$ nm). The structure of Au is face centered cubic ($Fm3m$, $a = 0.4079$ nm).

The first step for the preparation of the PbS/Cu_2O heterojunction was the electrodeposition of an epitaxial PbS film of about 0.5 μm thickness onto a Au(100) substrate. The deposition was carried out as described

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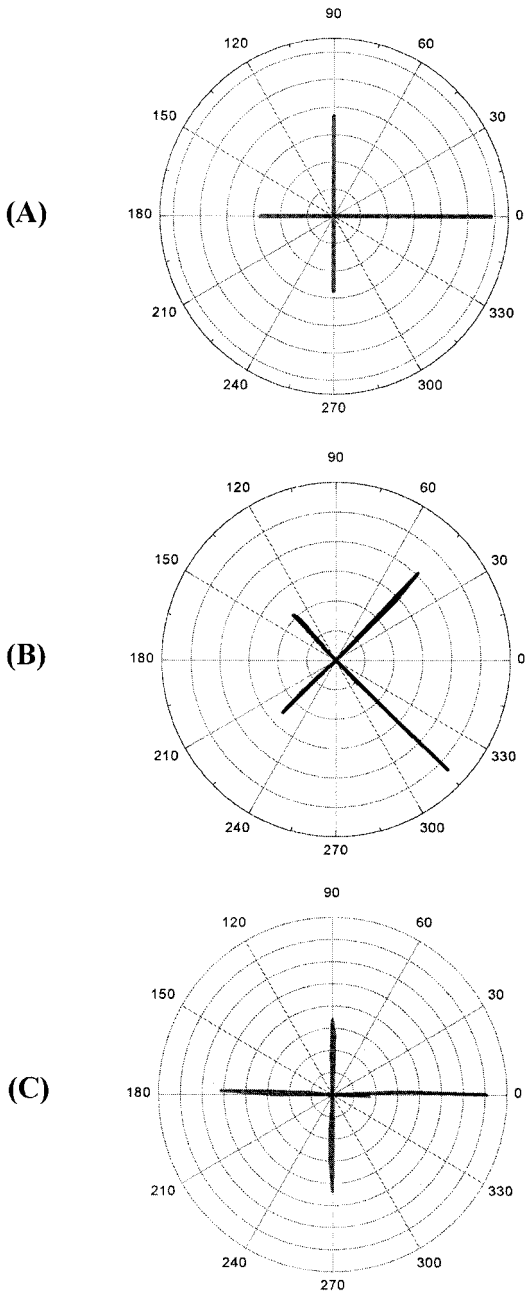

Figure 3. Azimuthal scans for (A) the (220) reflection of Au ($2\theta = 64.58°$), (B) the (220) reflection of PbS ($2\theta = 43.05°$), and (C) the (110) reflection of Cu_2O ($2\theta = 29.55°$). Each scan was acquired for the sample tilted 45° with respect to the plane of the goniometer. The (220) reflections for PbS are rotated 45° with respect to those of Au and Cu_2O. The average fwhm for the peaks are 0.5°, 1.6°, and 2.8° for Au, PbS, and Cu_2O, respectively.

elsewhere.[16] The sample was then rinsed with HPLC-grade water, dried, and immersed in the second deposition solution, which contained copper(II) lactate at pH = 9.0. The electrodeposition of the 0.5-μm-thick Cu_2O film was performed as described earlier.[15] Both films were deposited galvanostatically using current densities of 0.1 and 0.05 mA/cm^2 for the PbS and Cu_2O films, respectively.

X-ray diffraction (XRD) experiments were performed with a Scintag XDS-2000 diffractometer using Cu Kα radiation. Figure 2 shows the XRD pattern of the sample. Only the (200) and (400) reflections are observed for both deposited films, indicating an out-of-plane orientation. Because of the higher value of the atomic scattering factor for Pb atoms, the relative intensities of the (200) peaks for PbS and Cu_2O are significantly different although both films have the same nominal thickness.

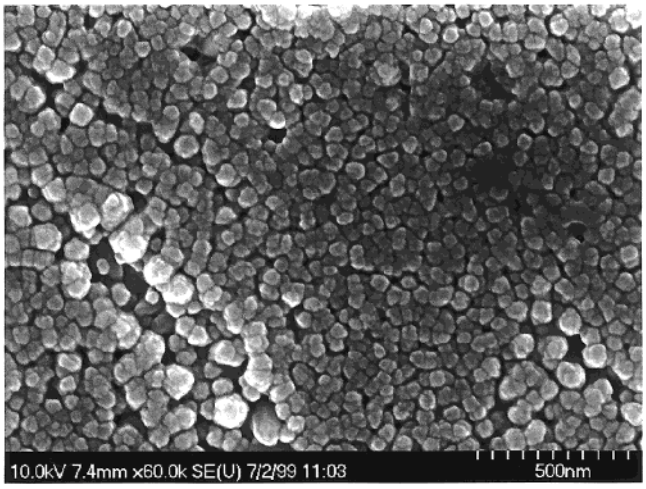

Figure 4. SEM micrograph of the Cu_2O overlayer. The SEM measurement was performed ex situ on an Hitachi model S4700 cold field emission scanning electron microscope.

Figure 3 shows the (220) azimuthal scans for Au and PbS and the (110) azimuthal scan for Cu_2O. The (110) reflection is symmetry-forbidden for Au (fcc structure), but allowed for Cu_2O (primitive cubic structure). Therefore, by choosing the (110) reflection of Cu_2O we avoid possible overlapping of the Au and Cu_2O peaks, so that the reflections observed in the azimuthal scan correspond to the film only. The expected 4-fold symmetry is observed in all three azimuthal scans in Figure 3. However, the (220) reflections of PbS appear at azimuthal angles rotated 45° with respect to the reflections of Au and Cu_2O. This means that although the PbS layer adopts the same (100) out-of-plane orientation as the substrate, the PbS structure is rotated 45° in plane with respect to the Au. An interface model consistent with this rotation is Au (100)/($\sqrt{2}\times\sqrt{2}R45°$)−PbS (100). Formation of this coincidence lattice decreases the large lattice mismatch between PbS and Au (45.5%) to +2.9%. The lattice mismatch between the second and the third layers is −38.9%. To accommodate this large mismatch, the cuprous oxide layer rotates 45° more in the plane of the substrate. The interface model of this junction is PbS (100)/($\sqrt{2}\times\sqrt{2}R45°$)−$Cu_2O$ (100), and the lattice mismatch is +1.8%. Thus, all crystallographic directions of the Cu_2O film coincide with those of the substrate, as we observed previously in the case of electrodeposition of individual Cu_2O films on the Au(100) single crystal.[15]

An SEM micrograph of the Cu_2O layer is shown in Figure 4. The SEM view of the lead sulfide underlayer is similar to that presented in ref 16 and contains smooth rectangular features. The cuprous oxide film consists of unfaceted grains with the size of about 50 nm. Since the film thickness is ∼10 times larger than the average grain size, we suppose that the Cu_2O film has a columnar structure with each individual column growing epitaxially on top of PbS. Cross-sectional electron microscopy of these materials is in progress to

verify this columnar structure and to determine the abruptness of the Cu_2O/PbS interface.

The particulate structure of the Cu_2O layer in the heterojunction is not ideal for the production of layered nanostructures, but it may be desirable for dye-sensitized photoelectrochemical cells, since the semiconductor−solution interfacial area should be large. Grätzel and co-workers have produced efficient photoelectrochemical cells based on dye-sensitized nanoporous TiO_2,[17] and Hara and co-workers have reported the photosplitting of water on nanocrystalline Cu_2O.[18] The Cu_2O in the present work should have the high surface area of a particulate semiconductor, but the epitaxial nature of the layer should provide more effective charge transport for the photogenerated carriers.

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