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Thin-film quantization studies of grey tin epitaxially grown on CdTe(111)

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Grey-tin thin films were successfully grown on clean single-crystal CdTe(111) under ultrahigh-vacuum conditions. Normally, bulk grey tin is a zero-gap semiconductor. However, in thin-film form, a band-gap opening was observed using high-resolution electron-energy-loss spectroscopy, the magnitude of which is thickness dependent. For example, as the grey-tin thickness varies from ~50 to 80 Å, the band gap varies from ~420 to 230 meV. The existence of such band gaps is attributed to quantum effects of carrier confinement within the grey-tin layer. From such thickness variation, we show from a simple one-dimensional potential model that the electron-confining potential at the CdTe/grey-tin interface is about 0.5 eV. This agrees very well with the value obtained by ultraviolet photoelectron spectroscopy.

I. INTRODUCTION

When a particle is confined in a one-dimensional square-well potential, its ground-state energy depends on the extent of the confinement. Tunneling studies by Chang, Esaki, and Tsu[1] and optical-absorption studies by Dingle, Wiegmann, and Henry[2] on GaAs-$Al_xGa_{1-x}As$ heterostructures demonstrated the existence of quantum levels due to such carrier (electron and hole) confinement in thin semiconductor films. Therefore, the effective band gap in semiconductor films increases with decreasing film thickness. These results have been exploited in single and multiple thin-layer semiconductor heterostructure light-emitter and laser devices.[3,4]

Therefore, if one starts with a zero-gap semiconductor, it would be possible to fabricate a semiconductor with a thickness-dependent band gap with a lower limit of zero. As is well known, tin can exist in two crystallographic forms: grey (α) and white (β). White tin has a tetragonal structure and is metallic. Grey tin has a diamond structure and is generally accepted to be a symmetry-induced zero-gap semiconductor.[5,6] In the bulk form, it is stable only below 13.2 °C. Recently, it has been demonstrated by Farrow *et al.*,[7,8] that Sn films grown on clean InSb (zinc-blende structure, $a=6.4798$ Å at 25 °C) or CdTe (zinc-blende structure, $a=6.4829$ Å at 25 °C) under ultrahigh-vacuum conditions assumed the lattice-matched diamond structure of grey Sn ($a=6.4898$ Å) at room temperature instead of the thermodynamically stable white Sn. Further, films up to 0.5 μm remained in the α phase at temperatures as high as 70 °C before the α- to β-Sn transformation took place. Therefore, grey-Sn thin films can be grown and substrate stabilized well above room temperature. Their work encourages the exploration of the aforementioned quantum-size effect in grey-Sn thin films. If a thickness-dependent band gap exists in grey-Sn films, potential applications as microwave and infrared devices may be realized.

In this paper, we present evidence for the existence of a finite band gap in grey-Sn films epitaxially grown on CdTe(111) as a function of film thickness, using the technique of high-resolution electron-energy-loss spectroscopy (HREELS). Ultraviolet photoelectron spectroscopy (UPS) was also used to determine the valence-band discontinuity at the CdTe/grey-Sn heterojunction. These results are then interpreted in terms of a simple one-dimensional potential-well model.

II. EXPERIMENTAL SECTION

High-resolution electron-energy-loss experiments were done in an ultrahigh-vacuum chamber equipped with a HREEL spectrometer, low-energy electron-diffraction (LEED) optics, ion sputtering capability, and a tungsten evaporator as shown in Fig. 1. The HREEL spectrometer was constructed in our laboratory and is similar to that developed by Froitzheim and Ibach[9] and modified by Sexton.[10] Photoemission experiments were done in a separate ultrahigh-vacuum chamber equipped with a helium lamp, a double-pass cylindrical mirror analyzer, and other similar standard facilities for specimen preparation.

CdTe(111) wafers (n type, resistivity=9.57 Ω cm) in 1-cm^2 disc shape as polished by the manufacturer (Eagle-

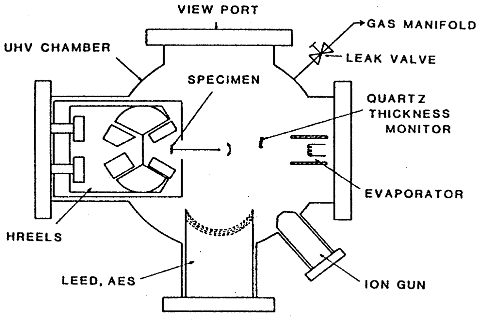

FIG. 1. Schematic diagram of the experimental setup.

Picher Ind.) were used in all experiments. Prior to loading into the vacuum chamber, the wafer was etched by 2% Br in methanol. The wafer was cleaned in ultrahigh vacuum by argon sputtering at 500 eV (current density $\sim 10^{-5}$ amp/cm^2) for 10 min, followed by annealing at 300 °C for 30 min. This specimen preparation procedure is close to that of Farrow *et al.*[7] Conventional tungsten filament evaporation was used for the deposition of tin (99.9995% pure from Materials Research Corporation). The thickness of the deposited tin layer was monitored by a calibrated quartz-crystal thickness monitor. The deposition rate was about 0.2 Å/sec. The background pressure was $\sim 2\times10^{-9}$ Torr during evaporation. The substrate temperature was about 20 °C during film growth. The LEED pattern was occasionally checked before and after film growth. After the deposition, the substrate temperature was kept at room temperature throughout the rest of the experiment. The pressure was typically $3-5\times10^{-10}$ Torr after deposition.

In HREELS studies, a monoenergetic electron beam (full width at half maximum $\sim$25—45 meV) was directed onto the specimen at an angle of 60° and an impact energy of 3—10 eV. The scattered electrons were collected in the specular direction and energy analyzed. The elastic peak count rates were typically 5×10^4 to 5×10^5 c/s.

III. RESULTS

After sputter annealing, the CdTe surface showed a sharp (1×1) LEED pattern. The surface was also found to be contamination free within the sensitivity limit of Auger spectroscopy (a few percent of a monolayer). After tin deposition, LEED showed a spot pattern (with somewhat higher background) of symmetry the same as that of the CdTe substrate indicative of the epitaxial growth of α-Sn of CdTe. In the thickness range we worked on (from about 50 to 200 Å), no Cd and Te Auger signals were observable after tin deposition.

Figure 2 shows the energy-loss spectrum of 200, 76, and 47 Å α-Sn grown on CdTe(111). In all spectra, loss bands peaked about 370—375 meV are due to carbon-hydrogen stretching vibrational losses of hydrocarbons adsorbed on the α-Sn surface during data acquisition. In addition, loss onsets whose energy positions were dependent on the thickness of α-Sn were observed. For example, the loss-onset energy is approximately 230 meV for 76 Å α-Sn and 420 meV for 47 Å α-Sn. Note that no such onsets were found in this energy range for 200 Å α-Sn on CdTe. Figure 3 shows the variation of the loss-onset energy as a function of α-Sn film thickness. The onset energy is found to decrease with increasing α-Sn film thickness. Note that these loss onsets are independent of the electron impact energy used in HREELS experiments.

He I UPS spectra of a clean CdTe(111) surface, 1, 6, and 40 Å α-Sn on CdTe are shown in Fig. 4. The Fermi level E_F was determined from the Fermi cutoff of a clean gold standard. With increasing thickness of α-Sn, the valence-band emission from α-Sn overlaps with that from CdTe. In the range 1—6 Å α-Sn on CdTe, the valence-band maximum of CdTe was located to be 1.1 ±0.1 eV below the Fermi level. After deposition of 40 Å α-Sn, the spectrum is completely dominated by the valence-band emission from α-Sn.

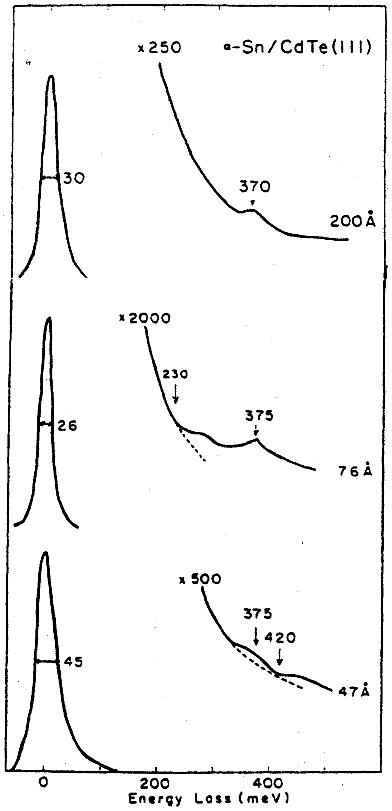

FIG. 2. Electron-energy-loss spectra of 200, 76, and 47 Å α-Sn grown on CdTe(111). The electron impact energy (uncorrected for work-function differences) is 5.5 eV for 200 Å, 8 eV for 76 Å, and 3 eV for 47 Å.

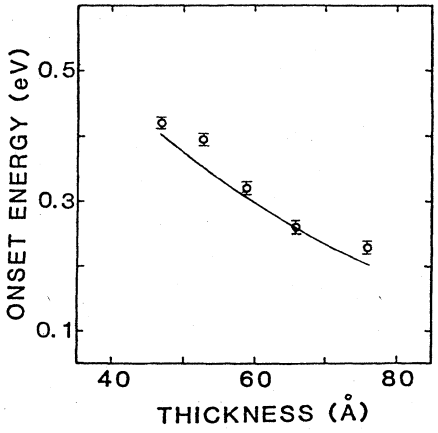

FIG. 3. Onset energy of loss bands as a function of α-Sn film thickness on CdTe(111). The solid line is the theoretical curve assuming an electron-confining potential well in α-Sn of depth 0.5 eV (see text for detail).

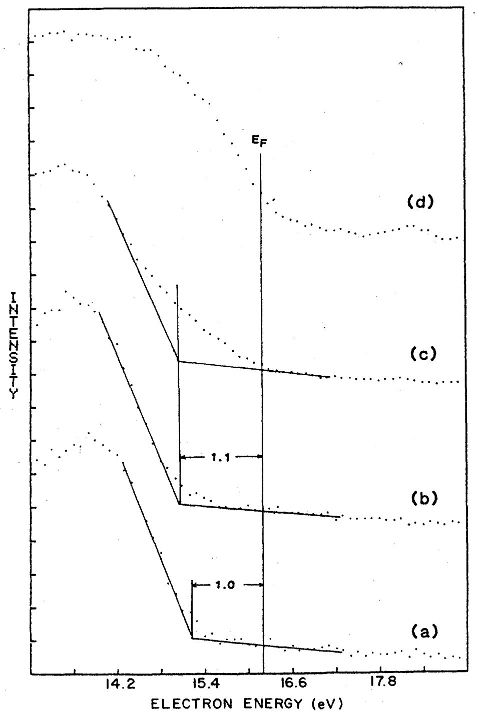

FIG. 4. He I UPS spectra of (a) clean CdTe(111), (b) 1 Å α-Sn on CdTe, (c) 6 Å α-Sn on CdTe, and (d) 40 Å α-Sn on CdTe. The emission beyond the Fermi level is due to excitation from the He II line. The overall energy resolution in these measurements is about 0.3—0.4 eV.

IV. DISCUSSION

The fact that the energy-loss-onset features are thickness dependent rules out artifacts such as impurity adsorption. The possibility that intermixing between CdTe and α-Sn gives rise to a semiconductor with band gap dependent on their relative concentration is also ruled out because we did not observe any Cd and Te Auger signals beyond an α-Sn thickness ~ 50 Å. Instead, these loss-onset features can best be explained by the formation of two-dimensional subbands in the α-Sn layer as a result of the quantum-size effect. To pursue along this line, we calculated the ground-state energy of the conduction band and the valence band assuming a potential diagram as shown in Fig. 5, simulating a thin layer of α-Sn on CdTe. For simplicity, the height of the well on the vacuum side was taken to be infinite for both valence and conduction bands. The potential at the CdTe/α-Sn interface was finite and assumed to be abrupt. The energy level for this half-infinite potential is well known and given by the equation

$$[(V-E)/E]^{1/2} = -\cot(2m^* L^2 E/\hbar^2)^{1/2} ,$$

where V is the height of the well and L the thickness of the well. The other symbols have their usual meanings. Assuming the conduction-electron and hole effective masses to be $0.0236m_0$ (Ref. 11) and $0.23m_0$ (Ref. 12), respectively, a good fit to the data shown in Fig. 3 was obtained by setting the electron well depth to 0.5 eV. The resultant band gap, which is equal to the sum of the ground-state energy of the conduction and valence bands, is shown as a function of α-Sn thickness by the solid line in Fig. 3. Because of the slight lattice mismatch between CdTe and α-Sn, a slight uniaxial Poisson dilation of α-Sn in the direction perpendicular to the film thickness is expected. However, the effective change in the band gap caused by this dilation is small (<10 meV) (Ref. 5) and is neglected in the present calculation. In Fig. 5, we assume that the potential in CdTe is constant although actually a band-bending or depletion region exists. Since the extent of the depletion region is much greater than the α-Sn thickness used in our experiments, we believe that the assumption is valid. Figure 3 shows that onset energies observed in HREELS track the theoretical curve fairly well.

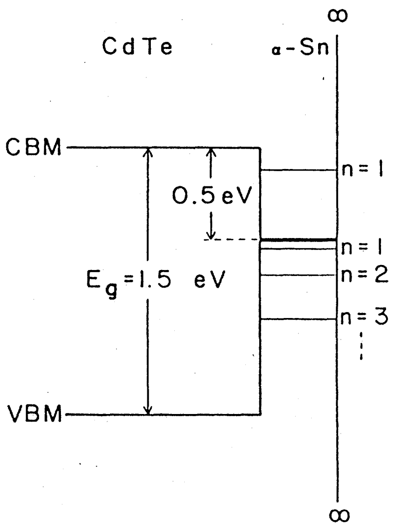

FIG. 5. Potential diagram for an α-Sn film grown on CdTe. The CdTe/α-Sn interface is assumed to be abrupt. CBM, conduction-band minimum; VBM, valence-band maximum.

For the given electron-confining potential of 0.5 eV, we found from the calculation only one bound electron state ($n=1$) in the conduction band for α-Sn thickness between 47 and 76 Å. We did not observe transitions from $n>1$ valence state to the $n=1$ conduction-band state. This may be due to selection rules operative in electron-energy-loss spectroscopy.[13]

In Fig. 4, one can locate the valence-band maximum of clean CdTe(111) by extrapolation to be at 1.0±0.1 eV below the Fermi energy. After deposition of 1—6 Å of α-Sn of CdTe, the valence-band maximum of CdTe shifts to 1.1±0.1 eV below the Fermi energy. Literature studies of metal-semiconductor and semiconductor-semiconductor heterojunctions show that band bending at such an interface should saturate at or below an overlayer thickness of one monolayer.[14,15] Our present determination of the valence-band maximum position of CdTe at 1—6 Å of α-Sn should thus be representative of the position at larger α-Sn thickness. It is interesting to note from Fig. 4(d) that the density of states at the Fermi energy after 40-Å tin deposition is essentially zero. This is an indirect evidence that we are not forming metallic (β) tin in our experiments.

As discussed earlier, a conduction-band well depth in α-Sn of 0.5 eV was deduced from HREELS studies. Since the band gap of CdTe at room temperature is 1.5 eV, this implies that the valence-band discontinuity at the CdTe/α-Sn interface is 1.0 eV. This is consistent with the present UPS results, where the corresponding valence-band discontinuity was found to be 1.1 ± 0.1 eV. The linear combination of atomic orbitals result of 1.28 eV by Harrison[16] also falls in the right range. This general agreement is encouraging, considering the simplicity of the model.

We have also performed some preliminary experiments on the α- to β-Sn transformation in such a system. We measured the electron reflectivity of the CdTe/α-Sn sample (i.e., the specular elastic peak intensity at constant monochromator settings) as a function of sample temperature. For samples prepared in these experiments, the reflectivity showed a sudden drop above a certain transition temperature. The transition temperature ranged from 60 to 80 °C in our samples and did not show any definite correlation with the α-Sn thickness. We interpret this reflectivity drop as the α- to β-Sn transformation. The basis for this interpretation is that the transformation converts an epitaxial and relatively smooth α-Sn layer into an incoherent and rougher β-Sn layer which hence exhibits lower reflectivity. This preliminary work clearly supports the observation of Farrow *et al.*,[7,8] on the enhanced temperature stability of α-Sn grown epitaxially on CdTe.

V. CONCLUSION

HREELS was applied to the observation of band-gap transition in 47 to 76 Å α-Sn film grown on CdTe(111). The energy-loss spectra show loss onsets with energy dependent on the thickness of α-Sn. The loss-onset energy agrees well with calculations using a simple one-dimensional quantum-well model, suggesting that α-Sn thin films grown epitaxially on CdTe attain a finite band gap because of carrier confinement.

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