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Photoluminescence of HgTe/CdTe superlattices under high hydrostatic pressures

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We have measured the photoluminescence (PL) of HgTe/CdTe superlattices under high hydrostatic pressures up to 30 kbar at liquid-nitrogen temperature. We observed several photoluminescence peaks with energies ranging from ~ 130 to ~ 700 meV. The most prominent peak at ~ 130 meV, which has been attributed to the recombination across the superlattice band gap, moves higher in energy with a pressure coefficient of $\lesssim 1$ meV/kbar. Other peaks, whose origins are not well established, have higher energies and their pressure coefficients are in the range of 0–2 meV/kbar. A calculation based on the envelope-function approximation gives a pressure coefficient of at least ~ 6.5 meV/kbar for the superlattice band gap. This is far outside the error bars of the measured pressure dependence of the main peak, $\lesssim 1$ meV/kbar. Varying the input parameters for the calculation, including the valence-band offset, changes the result of the calculation by less than 10%. Possible explanations for this disagreement, including a modification of the current model of HgTe/CdTe superlattice bands and a reinterpretation of the PL peaks, are examined.

I. INTRODUCTION

HgTe/CdTe superlattices (SL's) have been studied extensively since these structures were suggested as improved infrared detector materials for the 10-μm range of the spectrum.[1] Photoluminescence (PL) experiments have often been used to measure the band gaps of these SL's and to compare them with the results of theoretical calculations. There have been reports of several PL peaks from HgTe/CdTe SL's ranging in energy from ~ 100 meV to ~ 2.5 eV.[2–7] The most prominent peak at ~ 100–200 meV (or ~ 6–12 μm) observed in samples with HgTe and CdTe layer thicknesses of ~ 50 Å has been ascribed to transitions across the fundamental SL energy gap. In most cases,[3,4,6,7] these PL peak energies were close to the SL band-gap energies calculated with several different theories, including the most commonly used method, the envelope-function approximation (EFA). Also, absorption spectra and photocurrent spectra gave band-gap energies close to the PL peak energies. However, this identification has not been tested by using an external variable that changes continuously the input parameters of the theories.

One such variable is hydrostatic pressure, which changes continuously the bulk band structures of the constituent materials of the SL's. If the effects of pressure on the intrinsic bulk band structures of the constituent materials and the valence-band offset (Λ) between them are known, the effect of pressure on the SL band structure can be obtained within the EFA, which uses only bulk parameters and Λ as inputs. The EFA has been very successful in describing the electronic band structures of the GaAs/Al$_{0.3}$Ga$_{0.7}$As system at ambient and high pressures with the assumption that Λ is independent of pressure. For HgTe/CdTe SL's, the band structures of HgTe and CdTe and their dependences on pressure are well known and the value of Λ, which was a focus of controversy for some time, is generally accepted to be ~ 350 meV since Johnson, Hui, and Ehrenreich proposed a possible resolution of the controversy within the EFA.[8] Therefore, the pressure dependences of the PL peak energies of HgTe/CdTe SL's determined experimentally can be compared with the band-gap energies calculated within the EFA. Similar approaches have been very useful in testing theories for the GaAs/Al$_{0.3}$Ga$_{0.7}$As system. (For example, the valence-band offset value[9] and the Γ-X band mixing[10] of the GaAs/Al$_{0.3}$Ga$_{0.7}$As system were determined by high-pressure experiments.) In this paper we report a measurement of the PL of HgTe/CdTe superlattices under hydrostatic pressure, using pressures up to 30 kbar at 80 K.

As illustrated in Fig. 1, HgTe is a semimetal at ambient pressure, with the Γ_6 state lying 0.3 eV below the degenerate Γ_8 states. Pressure moves the Γ_6 state up in energy with respect to Γ_8. There have been several determinations[11] of the pressure coefficient of $E_{\Gamma_6}-E_{\Gamma_8}$ up to ~ 10 kbar, and their values cluster around 12 meV/kbar. If we extrapolate at this rate, the Γ_6 state would become higher in energy than the Γ_8 states and HgTe become a semiconductor with a finite-energy gap at ~ 25 kbar. CdTe is a direct-gap semiconductor with a pressure-dependent band-gap energy of

$$E_g = E_{\Gamma_6} - E_{\Gamma_8} = E_0 + \alpha P + \beta P^2 , \tag{1}$$

where $E_0 = 1.58$ eV, $\alpha = 8.6\times 10^{-3}$ eV/kbar, and $\beta = -4.8\times 10^{-5}$ eV/kbar^2 at 80 K.[12] It is known that bulk HgTe undergoes a structural phase transition from the zinc blende to the hexagonal cinnabarlike structure at

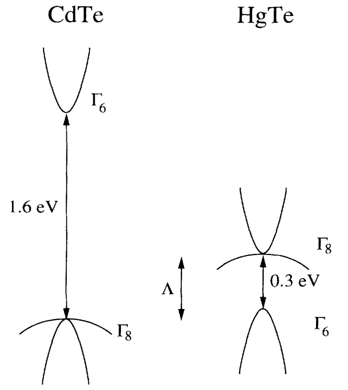

FIG. 1. Schematic of the bulk band structures of CdTe and HgTe and their relative lineup in superlattices at atmospheric pressure. Valence-band offset (Λ) value of 350 meV is used.

~13 kbar at room temperature.[13] This could limit the maximum available pressure range to ~13 kbar. In a SL structure, however, the phase transition of the HgTe layers is expected to be suppressed until the CdTe layers undergo their phase transition[14,15] from the zinc blende to the NaCl-like structure at ~39 kbar.[12] Above the bulk HgTe phase-transition pressure, the SL structure might have strain due to the suppression of the phase transition of the HgTe layers.

II. EXPERIMENT

The sample was grown by molecular-beam epitaxy at North Carolina State University. The sample consists of 200 periods of HgTe and $Hg_{0.15}Cd_{0.85}Te$:As layers deposited onto a (211) $Cd_{1-x}Zn_xTe$ ($x \sim 0.04$) substrate. The thicknesses of the layers are 45 and 61 Å, respectively. The sample was cut with a diamond wire saw to a $\sim 5\times 5$ mm square, thinned down to a thickness of ~65 μm, and then cleaved to a dimension of $\sim 250\times 150$ μm. Since this material is known to be very unstable, extreme care was taken in handling and processing the sample. PL spectra taken before and after the cutting and the thinning showed no change in the peak energy or the width of the peak due to these processes. The sample, together with ruby chips for determining pressure, was then loaded into a NBS-type[16] diamond-anvil cell (DAC) with a pressure compartment of ~450 μm in diameter and ~100 μm in depth. Since type-Ia diamonds, used in most DAC's, are opaque in the 7–11-μm range,[17] an infrared-transparent type-IIa diamond was used for the front side anvil. As a pressure medium we used a 4:1 mixture of methanol:ethanol, which has been shown to be adequate for cryogenic experiments if the pressure is changed at room temperature.[18] The cell was mounted in a liquid-nitrogen cold finger dewar. The 5145-Å line of an argon-ion laser, modulated by an optical chopper at 800 Hz and focused to a beam diameter of ~100 μm with a power density of 2×10^2 W/cm^2 at the sample, was used as excitation radiation. The luminescence was dispersed by a Jarrell-Ash half-meter grating monochromator and detected by an Infrared Associates mercury-cadmium-telluride detector cooled with liquid nitrogen. A KRS-5 crystal was used to prevent scattered laser light from entering the monochromator. The sample and the ruby chips in the pressure compartment were monitored *in situ* with a telescope through the back side anvil. The detector signal was processed using a preamplifier and a lock-in amplifier and recorded by a computer. For each luminescence measurement the pressure was changed at room temperature and the value determined at 80 K.

III. RESULTS

Figure 2 shows typical PL spectra from the sample inside the DAC at 11.1 and 20.4 kbar at 80 K. Three major PL peaks are observed and the strongest peak is at ~130 meV. This peak is the one that has been ascribed to the SL band-gap transitions.[3,4,6,7] The origins of the other two peaks are not clear. In order to make sure that these peaks do not originate from the $Hg_{0.15}Cd_{0.85}Te$ barrier material or the $Cd_{0.96}Zn_{0.04}Te$ substrate, PL spectra of a $Hg_{0.15}Cd_{0.85}Te$ epilayer grown on a CdTe substrate and a $Cd_{0.96}Zn_{0.04}Te$ wafer were taken and these peaks were found to be absent. Higher-energy PL peaks from HgTe/CdTe SL's have been reported[5,7] and they have been ascribed to the transitions between higher-energy SL minibands. However, since most of the photoexcited carriers relax to their lowest-energy states before they recombine, these higher-energy transitions are not expected to be observable in low-temperature PL spectra. Therefore, we will focus on the strongest peak at the lowest energy. The shape and the intensity of this peak

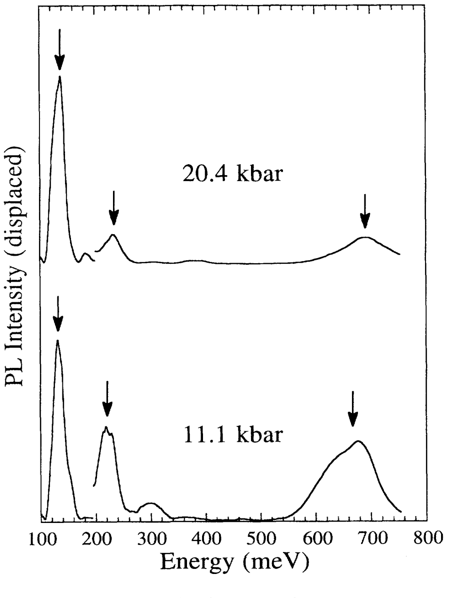

FIG. 2. Typical infrared photoluminescence spectra of the sample inside the DAC at 11.1 and 20.4 kbar. Three most prominent peaks are indicated by arrows. Different gratings were used for different wavelength ranges and the spectrum for each range is normalized to give correct relative peak intensities.

change somewhat with pressure, though the peak energy changes less than 10 meV over the 30-kbar pressure range, as shown in Fig. 3. We estimate the pressure coefficient of the energy of this peak to be < 1 meV/kbar. There is no indication of a phase transition of the HgTe layers at ~13 kbar. These results were confirmed with another sample from the same wafer. When the pressure was raised to ~35 kbar at room temperature and 31 kbar at 80 K, the epitaxial surface of the sample showed cracks indicating a structural phase transition of the SL layers. Above this pressure the PL was not observed.

The pressure dependence of the SL fundamental energy gap has been examined theoretically with an envelope-function approach based on the eight-band Kane model. The parametrization of the band structures in bulk HgTe and CdTe is similar to that which has been previously employed to describe the optical properties of HgTe/CdTe SL's.[19] Initial calculations were conducted using $\Lambda = 350$ meV (Ref. 20) and the assumption that Λ was pressure independent. The small effects of strain due to the pressure-dependent lattice mismatch between HgTe and CdTe were also incorporated in the calculation. The possible structural phase transition of HgTe above 13 kbar was not taken into account, so the calculations may be considered less reliable above this pressure. The solid curve in Fig. 3 indicates the calculated SL band-gap energy as a function of pressure. The band-gap energy increases at a rate of ~6.5 meV/kbar near zero pressure and this rate increases to ~8 meV/kbar when the pressure reaches 20 kbar. The sensitivity of the calculated pressure dependence of the energy gap to the input parameters, within their ranges of uncertainty, has been examined. A small offset value ($\Lambda = 40$ meV) changes the energy of the gap at zero pressure to ~210 meV, but the pressure dependence is still ~6 meV/kbar. Similarly, other input parameters may vary the value of the gap significantly but do not significantly alter the pressure dependence. The overall uncertainty of the pressure dependence of the gap due to the uncertainties of the input parameters is estimated to be less than 10%. The behaviors of the next-lowest-energy optically allowed transitions in the SL have also been examined and they are shown in Fig. 3 by dashed curves. These transitions energies have pressure dependences similar to that of the fundamental energy gap. We note that the calculated energies for the three lowest optical transitions at zero pressure are close to the energies of the three most prominent peaks in our PL spectra, though PL from the two higher-energy transitions would not be expected to be observable at 80 K.

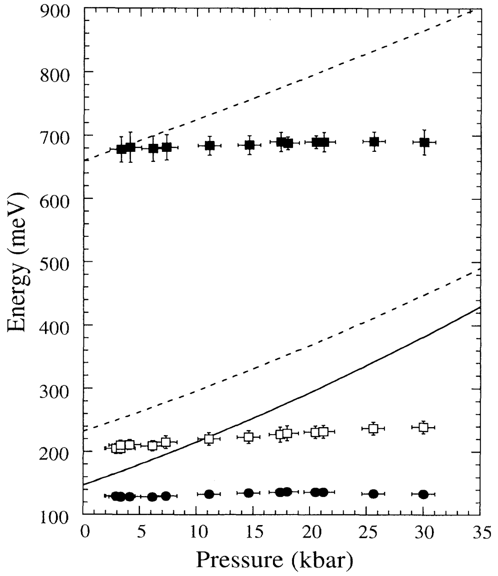

FIG. 3. Pressure dependences of the three most prominent photoluminescence peaks in the 100–750-meV range at 80 K. All three peaks have pressure coefficients of <2 meV/kbar. The solid curve indicates the pressure-dependent SL band-gap energy calculated within the EFA. The calculated band-gap energy has a pressure coefficient of at least 6 meV/kbar. The dashed curves indicate the pressure dependence of the next-lowest-energy optically allowed transitions.

IV. DISCUSSION

The pressure dependence of the SL band gap of > 6 meV/kbar, calculated in the EFA, is far outside the error bars of the measured pressure dependence of the main peak, < 1 meV/kbar. Possible structural phase transitions or strain above 13 kbar cannot explain this disagreement because the data for pressures less than 12 kbar establish pressure coefficients of less than 1 meV/kbar for the main peak and less than 2 meV/kbar for the other peaks. The disagreement between theory and experiment suggests at least one of three possibilities. First, the EFA may be inappropriate to determine the band gap and its pressure dependence for the HgTe/CdTe SL's. This approximation has been very successful in determining the band gap and its pressure dependence for the GaAs/$\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ heterostructures, but there is still some controversy[21] over the validity of using the EFA for determining these parameters for the HgTe/CdTe SL's, in spite of its apparent success in describing the observed properties of the HgTe/CdTe SL's at atmospheric pressure.

Second, the assignment of the strong PL peak at atmospheric pressure to the fundamental SL band gap may be incorrect. Although the strong correlation between the PL peak energy and the HgTe layer thickness suggests that the PL is due to the transition across the SL band gap,[4] the reported discrepancy between the temperature dependences of the PL peak energy and the absorption edge[2] makes this assignment less definite. Because some of the SL bands are so-called "quasi-interface bands," which have large probability densities at the HgTe/CdTe interface where a large number of interface defects also exist, the fundamental PL may not be strong enough to be seen and the observed PL may be defect luminescence associated with the interface. This is supported by the existence of the higher-energy peaks. If this is the case, the PL of HgTe/CdTe may have been generally misidentified in the previous studies. Absorption measurements as a function of pressure would be a decisive test of this possibility.

Third, one of the assumptions ancillary to the use of the EFA may be incorrect. This could be the assumption that it is proper to ignore the possibility that a defected atomic arrangement at the HgTe/CdTe interface is determining one or other of the band-edge states. Alternatively, the assumption of pressure independence of Λ could be wrong. Even though it has been assumed to be valid,[4,9,22] with some theoretical support,[23] there has been no experimental proof. Also, there has been a suggestion of a temperature dependence of Λ.[24] Our calculations of the effect due to an assumed pressure dependence of Λ, however, indicate that to reduce the pressure dependence of the gap to 4 and 1 meV/kbar, Λ has to increase by 15 and 30 meV/kbar, respectively, which seem unreasonably high.

V. CONCLUSIONS

We have measured the PL of HgTe/CdTe superlattices as a function of pressure up to 30 kbar. The observed pressure dependence of the PL peak energy is much weaker than the pressure dependence of the SL band gap calculated within the EFA. The resolution of this discrepancy requires either a reinterpretation of the conventional assignment of the PL in this system, or a modification of the current theories based on the EFA.

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