

Near-band-gap photoluminescence of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$

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creased resolution. It was taken at the so-called "second-Scherzer" defocus (-140 nm for the Philips 301) where spatial periodicities in the range 0.3 – 0.55 nm are imaged strongly but with reversed contrast.

The line AB defines the interface between the substrate and the implanted layer. This is not noticeably different from the interface before laser irradiation.¹⁰ It can be seen that the first 12 nm or so of the amorphous layer to the northwest of AB contains no sign of crystallinity. After that there are several small crystallites visible, which just happen to have their 111 planes aligned with the beam direction. Note, however, the background contrast does not change character until approximately CD, where it becomes coarser. The fine detail of the background contrast arises from nearest-neighbor spacings in amorphous silicon. The coarser contrast is exhibited by surface roughness and contamination. Thus the existence of approximately 10 nm of intermediate amorphous and small-grain polycrystalline Si is confirmed by this image.

A first-order phase change has occurred in the topmost 60 nm of the implanted layer, resulting in the growth of large-grain polycrystals with a characteristic fan shape. This zone has presumably melted and recrystallized from the bottom up. No regrowth has occurred at the interface between the substrate and the amorphous layer but partial solid-state growth has occurred in the 10 nm immediately below the melted layer. Solid-state thermal regrowth rates do not appear to be quite sufficient to explain the size (about 5 nm) of the crystals in this region.¹ Within 50 °C of the melting point

it would require at least 50 ns (Ref. 11) to nucleate crystals of this size, whereas the measured liquid duration (from reflectivity) at this laser energy is much less than this. (In fact 0.2 J cm⁻² is the threshold for melting as measured by Auston and co-workers¹¹—50 ns surface duration of liquid is achieved only with three times this energy.) Presumably stress⁶ or ionization⁵ effects must be taken into account to explain the increased rate of growth. A fuller publication describing a whole series of irradiation doses on this sample, up to and above threshold, is now in preparation.

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Near-band-gap photoluminescence of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$

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The results of photoluminescence studies of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ with $x = 0.32$ and 0.48 for temperatures between 5 and 30 K are described. In the $x = 0.32$ and $x = 0.48$ material, band-to-band, band-to-acceptor, and donor-to-acceptor luminescence lines are observed. We report the first observation of bound-exciton luminescence in HgCdTe , which we observe in the samples with $x = 0.48$.

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The results of a series of photoluminescence experiments on $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ for samples with $x = 0.32$ and 0.48 are presented. We report the first observation of the luminescence from a bound exciton in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$. Other lines due to band-to-band, band-to-acceptor, and donor-to-acceptor transitions are also observed.

While $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ is an important material for infrared applications,¹ its luminescence properties have not been extensively investigated. Photo- and cathodo³-luminescence spectra have been measured by other groups for samples with $x = 0.3$. They observed two broad luminescence

lines which they attributed to band-to-band and band-to-impurity transitions.^{2,3} The impurity was thought to be Hg vacancies.³ Recently, Osbourn and Smith⁴ have suggested that radiative recombination should dominate nonradiative Auger recombination of bound excitons for $x > 0.4$. These results suggest that it should be easier to observe bound-exciton luminescence in high- x samples than in low- x samples.

Our luminescence experiments have been carried out on samples of two compositions, one of $x = 0.32$ with a band gap near 0.25 eV, and the other of $x = 0.48$, with band gap

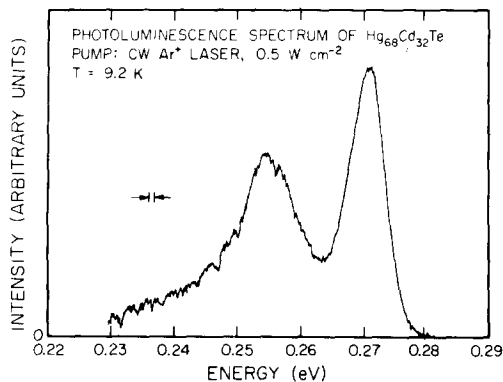


FIG. 1. Photoluminescence intensity vs energy of emitted photon for $\text{Hg}_{68}\text{Cd}_{32}\text{Te}$. The high-energy peak is attributed to a band-to-band transition. The low-energy peak is attributed primarily to donor-to-acceptor luminescence below ~ 10 K, and band-to-acceptor luminescence at higher temperature. The fine structure seen on the low-energy peak is due to absorption by water vapor.

near 0.5 eV. Spectra were measured for temperatures between 5 and 30 K and average pump power, provided by a mechanically chopped cw Ar^+ laser with 50% duty cycle, of between 0.5 and 14 W/cm^2 . Laser light was focused onto the sample, mounted in a Janis liquid-helium research dewar. A heater and temperature sensor mounted near the sample in the sample arm of the dewar allowed temperature control. The luminescence from the sample was dispersed with a monochromator and detected with either an InSb (for $x = 0.32$ material) or an InAs detector (for $x = 0.48$ material). The detector output was analyzed with a lock-in amplifier.

In the $x = 0.32$ samples, two broad luminescence bands are observed, as shown in Fig. 1. Two lightly p -type samples were studied, each grown by float-zone-refining polycrystalline HgCdTe , annealed in Hg vapor to reduce Hg vacancies, and doped with 10^{15} cm^{-3} Au atoms.⁸ The composition of these samples was determined by measuring the photoconductivity cutoff wavelength for a sample cut from the same boule adjacent to the sample we studied.⁸ The results of our experiments are similar for both our $x = 0.32$ samples.

The higher-energy line can be identified as a band-to-band transition by the variation in intensity with pump power, and energy shift with temperature. The peak intensity of the line divided by pump power increases as pump power is increased. As pump power is increased by a factor of 5, the ratio of intensity to pump power increases by 30% at 30 K and by 100% at 4.8 K. The peak of the line shifts to higher energy as the temperature is increased. At all pump powers, the energy shift is 7.5 meV in going from ~ 5 to ~ 30 K, of which only ~ 4.5 meV is due to band-gap shift.¹ These observed properties are consistent with the interpretation of the line originating in a band-to-band transition.⁵ The ratio of intensity to pump power increases with pump power because of the saturation of centers that bind carriers. The energy shift with temperature (over that caused by band-gap shift) comes about because higher-lying free-electron and hole states are filled as the temperature increases.

The lower-energy line in Fig. 1 has a different appearance and behavior from the higher-energy line. It is distinctly asymmetric, having a long low-energy tail. While the

asymmetry is not particularly evident in the 9.2-K spectrum given in Fig. 1, the asymmetry is evident in lower-temperature spectra ($T \sim 5$ K) where the band-to-band line is less intense. This line is also wider than the higher-energy line, having a full width at half maximum of 13 as opposed to 7 meV. The intensity of this line does not increase with pump power as rapidly as the band-to-band line. The peak energy shifts like the band gap from 5 to 10 K, then shifts 2 to 4 meV (depending on pump power) more than band gap from 10 to 30 K.

These properties suggest that the lower-energy line is due to donor-to-acceptor luminescence⁶ at low temperatures and is produced by a free electron recombining with a bound hole⁷ at higher temperatures when the donors are ionized. The observed intensity variation with pump power supports the interpretation of the line as involving a bound hole: as the centers become saturated, both donor-to-acceptor and free-to-bound line intensities should decrease in relation to a free-to-free line intensity. The observed shift in energy of the line indicates a change from a transition involving only bound carriers at low temperature to one involving a free carrier at the higher temperatures studied. This change is indicated because, if the lower energy line is produced only by donor-to-acceptor luminescence, the line peak would shift at approximately the same rate as the band-gap energy as temperature is increased, for the entire temperature range.

In the $x = 0.48$ material, three luminescence lines (a spectrum is shown in Fig. 2) are observed in two of our samples. One of these samples is lightly p type, with 10^{16} cm^{-3} Au atoms.⁸ The other is lightly n type, with 10^{15} cm^{-3} donors.⁸ In the third $x = 0.48$ sample studied, only the low- and high-energy lines are observed. This sample is p type, with 10^{15} cm^{-3} Au atoms.⁸ All three samples were grown using the solid-state recrystallization method, and were annealed in Hg vapor to reduce the concentration of Hg vacancies.⁸ The composition of these samples was determined by the amount of the constituents put into the melt before it was quenched.^{8*}

The high-energy line is qualitatively similar to the corresponding line in the $x = 0.32$ material. The peak of the line shifts about 7 meV between 4.7 and 30 K in all samples of $x = 0.48$ material studied. As pump power is increased from

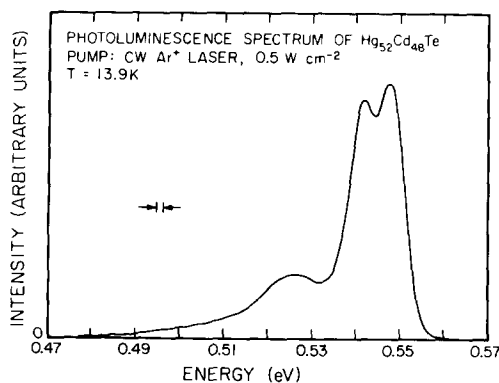


FIG. 2. Photoluminescence intensity vs energy of emitted photon for $\text{Hg}_{52}\text{Cd}_{48}\text{Te}$. The high-energy peak is attributed to a band-to-band transition. The low-energy peak is attributed primarily to donor-to-acceptor luminescence below ~ 10 K, and to band-to-acceptor luminescence at higher temperature. The intermediate-energy line is interpreted as bound-exciton recombination luminescence.

2 to 5 W cm⁻², the intensity of the line divided by the pump intensity increases by 30 to 100% (depending on temperature). This ratio of line intensity to pump intensity then stays the same, or decreases slightly as the pump power is increased to the highest pump power studied, 14 W cm⁻². These properties indicate that the line is produced by a band-to-band transition, for the same reasons given earlier for identifying the corresponding line in the $x = 0.32$ material.

The low-energy line in the $x = 0.48$ material is also similar to its counterpart in the $x = 0.32$ material. The line peak shifts to higher energy with increasing temperature above ~ 10 K, shifting 10 meV between 9.2 and 30 K at the lowest pump power, 2 W cm⁻². The peak does not shift with temperature below ~ 10 K, except for a small shift at the highest pump power studied. The ratio of the intensity of the low-energy line to the intensity of the high-energy line decreases with pump power, except that at 20 and 30 K the ratio increases as pump power is raised from 5 to 14 W cm⁻². Using the same argument given above for $x = 0.32$ material, we identify this line as donor-to-acceptor luminescence at low temperature, and free-to-bound luminescence at the higher temperature studied.

The intermediate-energy line appears only in some samples of the $x = 0.48$ material. The line peak does not shift with temperature to within 1 meV (the experimental uncertainty of the peak positions) between 4.6 and 18.8 K. Since the band gap for material of this composition shifts by less than 1 meV in this temperature range (Ref. 1, p. 29), the peak position is fixed with respect to the band gap for these temperatures. The line intensity falls off more rapidly with increasing temperature than either of the other lines, and is not visible in the spectra taken above 18.8 K. As pump power is increased, the line intensity increases at a rate that is slightly less than linear. The characteristics of this line suggests that it is produced by bound-exciton recombination. Since both the hole and electron are bound, the peak position should not change relative to the band gap with temperature. Also, the intensity should fall off rapidly with temperature as the centers are depopulated by thermal excitation of the excitons. Finally, the variation of intensity with pump power is also consistent with a bound-exciton interpretation, because the centers binding the exciton should saturate as the pump power is increased.

The position of this line is approximately that of donor-valence-band luminescence. There are several pieces of evidence that indicate that this is not the origin of the line. The most compelling argument is that donor-valence-band luminescence should shift to higher energies as the temperature is increased, and higher-energy hold states are occupied. Furthermore, the width is appropriate to a bound-exciton line. A donor-valence-band line should have a width of about 1 meV, while the observed line width is 6 meV, which is closer to the 4-meV width expected for a bound-exciton line.

The positions of the various lines provide donor and acceptor ionization energies. The difference in energy between the band-to-band line and the donor-acceptor line at zero temperature is a lower limit on the sum of the donor and acceptor energies. The acceptor energy is the difference be-

tween the band-to-band line and the band-to-acceptor line extrapolated to zero temperature. The overlap between the band-to-acceptor and donor-acceptor lines and errors associated with extrapolated to zero temperature cause some uncertainty in the procedure, but some limits may be estimated for the ionization energies. For the $x = 0.32$ material, the acceptor energy is 14.0 ± 1.5 meV, and for the donor, the ionization energy is less than 2 meV. For the $x = 0.48$ material, the two ionization energies are 15.5 ± 2 and 4.5 ± 2 meV, respectively. For comparison, the authors of Ref. 2 estimate values of acceptor ionization energy for $x \sim 0.3$ material of 13 meV from the luminescence data and 20 meV from the temperature dependence of the Hall data. For $x = 0.5$ material, they estimate 25 meV from luminescence measurements. While the agreement is not particularly good, the results are consistent with one another in light of the uncertainty involved.

In summary, we have shown spectra of near-band-gap photoluminescence from Hg_{1-x}Cd_xTe with $x = 0.32$ and $x = 0.48$, and presented our interpretation of the origin of the lines. The $x = 0.32$ material shows two lines. The properties of the high-energy line are consistent with those for a band-to-band transition, and those of the low-energy line with donor-to-acceptor luminescence at low temperature and free-electron to bound-hole luminescence above ~ 10 K. The $x = 0.48$ material shows both these bands, which we interpret similarly, plus an additional line which we attribute to bound-exciton recombination.

The presence of the bound-exciton luminescence in the $x = 0.48$ material is consistent with the Osbourn-Smith calculation showing a radiative efficiency of 90% for the bound exciton in HgCdTe of this composition. The absence of a corresponding line in the $x = 0.32$ samples cannot be taken as conclusive evidence that bound-exciton luminescence does not occur in this material, since we do not observe bound-exciton luminescence in one of the $x = 0.48$ samples we have studied. It is therefore possible that other mechanisms are responsible for the absence of bound-exciton luminescence, such as overlap of the bound exciton with too many impurities. This overlap would be more likely in $x = 0.32$ than in $x = 0.48$ material, because the exciton radius is larger in the $x = 0.32$ material. However, the absence of the bound-exciton luminescence in the $x = 0.32$ samples is consistent with the Osbourn-Smith estimate of a much lower radiative efficiency of 20% for the bound exciton in that material.

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⁸Sample characterization and preparation were carried out at the Santa Barbara Research Center, Santa Barbara, Calif. [P. Bratt and R. Cole (private communication)].

Double heteroepitaxy in the Si (111)/CoSi₂/Si structure

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Epitaxial growth of CoSi₂ films on Si substrates and the growth of Si films on the Si (111)/CoSi₂ structure are investigated. Solid phase epitaxy is used to grow both CoSi₂ and Si films. Molecular beam epitaxy is also used to grow the top Si films in the double heteroepitaxy. It has been found that two dominant factors required to obtain good epitaxial films are substrate cleaning by lamp heating before the film deposition and annealing of the deposited films without exposure to air. Excellent crystalline quality of the CoSi₂ films on (111) Si substrates and good quality of the Si films on the Si (111)/CoSi₂ structure have been demonstrated by ion channeling and backscattering techniques and reflection electron diffraction analysis. Uniformity of the grown films has also been examined by scanning electron microscopy.

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A monolithic semiconductor-metal-semiconductor structure is useful for such high-speed devices as the metal base transistor,¹ the permeable base transistor,² and the buried-metal-gate static induction transistor. This structure will also be important in research of the metal-semiconductor superlattice and three-dimensional integrated circuits. In order to realize this structure, it is necessary to grow a single-crystal-like semiconductor film onto a metallic film without interdiffusion between the films, which means that the semiconductor film must be grown at temperatures lower than the diffusion temperature of the metal atoms into the semiconductor. Though it was rather difficult to satisfy these conditions by the usual Si device technology, the recently developed solid phase epitaxial growth of Si (Ref. 3) and metal-silicide films^{4,5} has the potential to form a Si/silicide/Si structure. In fact, the formation of a Si (111)/Pd-silicide (epi)/Si/Pd-silicide (poly) structure by solid phase epitaxy has been reported.⁶ However, it seems to be difficult to use this structure for practical applications because of the large amount of residual Pd atoms in the grown Si film.

In this letter, we show experimental results on the single heteroepitaxy of CoSi₂ films on (111) and (100) Si substrates and the double heteroepitaxy of Si films on the Si (111)/CoSi₂ structure. In the double heteroepitaxy, the CoSi₂ films were formed on (111) Si by solid phase epitaxy (SPE), while the top Si films were formed by both SPE and evaporation of Si onto hot substrates [so-called molecular beam epitaxy (MBE)]. CoSi₂ has a cubic CaF₂ structure with $a = 0.537$ nm, and the mismatch of the lattice parameters with Si substrates is about 1.2%. Though this value is larger than the mismatch ($\sim 0.4\%$) between NiSi₂ and Si, CoSi₂ is consid-

ered more suitable as a metallic film in the double heterostructure because it has a higher melting point (1326 °C) than NiSi₂ (993 °C). The crystalline quality of the epitaxial films was characterized by means of the backscattering and channeling measurements with 1.5-MeV He ions and the reflection electron diffraction (RED) analysis with an electron energy of 50 keV. The channeling minimum yield χ_{\min} in the backscattering analysis is defined as the ratio of the aligned to the random yields at a portion just behind the surface peak in the Co and Si spectra for CoSi₂ and Si films, respectively. Scanning electron microscopy (SEM) was also used to examine the uniformity of the grown films.

In this work, 2–5- Ω -cm p -type (111) and (100) Si wafers were used. They were immersed in an RCA solution (H₂O₂:NH₄OH:H₂O = 1:1:5, 85 °C) for 15 min, etched in a 46% HF solution, immersed again in another RCA solution (H₂O₂:HCl:H₂O = 1:1:5, 85 °C) for 15 min, and then etched in a 10% HF solution. Finally, the samples were rinsed in high-purity water and immediately loaded in a vacuum chamber equipped with ion pumps, an electron beam evaporation system with three crucibles, and a furnace system with two 500-W halogen lamps and reflectors. The base pressure of the chamber was less than 3×10^{-7} Pa. Samples can be heated in the furnace up to about 1050 °C with a uniform-temperature area of about 2 cm². In the main growth process of this experiment, the furnace was used to clean the surface of Si substrates before film deposition (preheating) and to anneal the deposited films without breaking the vacuum (postheating). In order to check the contamination effect from air,⁷ some samples were kept in air for more than one day without postheating and then annealed in another vacuum furnace.