Three-dimensional quantum-size effect in chemically deposited cadmium selenide films

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Optical band gaps, E_g, up to 0.5 eV higher than in single-crystal samples, are observed for chemically deposited films of CdSe and explained in terms of a quantum-size effect, whereby the electrons are localized in individual crystallites. The increase in E_g depends strongly on deposition temperature, with the greatest increase obtained at the lowest temperature. Annealing at temperatures above the deposition temperature causes a decrease in E_g; this decrease is stronger at higher annealing temperature. Structural studies of the as-deposited layers showed them to be composed of microcrystalline, cubic CdSe, and electron microscopy resolved them into individual crystallites of typically 40–80-Å diameter, depending on deposition temperature. This is the first example reported of a three-dimensional quantum-size effect in a film.

I. INTRODUCTION

The three-dimensional quantum-size effect, leading to an increase in band gap with decrease in particle size, is well known for colloidal semiconductor sols where the individual colloidal particles are dispersed in a liquid or glass.[1] It is caused by localization of electrons and holes in a confined space (the colloidal particle) resulting in observable quantization of the energy levels of the electrons. This leads to an increase in the optical gap of the semiconductor when the particle dimensions become less than a critical size, which depends on the effective masses of the electron and hole and on the dielectric constant of the semiconductor. It is typically on the order of 4–10 nm.

The nature of this effect demands electronic isolation between particles (i.e., localization of charges to one particle). Thus when individual particles are in electrical contact, we might not expect to see such quantization effects. However, Fojtik et al. have obtained dried precipitates of CdS showing this effect;[2] they explain this by the presence of a surface layer of some foreign material on the CdS particles which prevents electronic contact between them.

Chemical deposition is a well-known method for preparing semiconductor layers and has been used mainly for metal sulfides and selenides. Due to the interest in CdSe over the past decade, which has been generated largely by its potential use in photoelectrochemical cells, simple methods of preparing CdSe layers have been investigated by many groups; chemical deposition is one of these.[3]

In most cases of chemically deposited (CD) CdSe studied to date, the CdSe layers have been annealed—usually to ~500 °C in air—in order to optimize photoelectrochemical performance. Relatively little attention has been paid to the properties—other than morphology—of the as-deposited layers. The main exception to this is a study by Kainthla et al. of the optical and structural properties of as-deposited CdSe.[4,5] They found, using electron diffraction, that the structure of the film deposited from a clear solution, i.e., without $Cd(OH)_2$ in suspension, was predominantly cubic, while from a turbid [with $Cd(OH)_2$] solution it was mixed cubic and hexagonal. Using optical transmission measurements they measured a band gap of 1.74 eV; electron microscopy showed the film to have a pebbly, polycrystalline morphology with a grain size of ~600 Å. Boudreau and Rauh[6] note that their as-deposited films of CdSe were red. Rajeshwar et al.[7] measured a resistivity for as-deposited CdSe films of ~10^7–10^8 Ω cm, which dropped to 1–10 Ω cm after annealing at 280 °C in vacuum.

We describe here optical and photoluminescence spectra, x-ray and electron diffraction studies, transmission electron microscopy and elemental analyses, together with some preliminary (photo)electrical characterization of non-annealed CD CdSe layers, and show that the difference between these layers and "normal" CdSe (i.e., with properties similar to large-grained or single-crystal materials which have a room-temperature band gap of 1.73 eV) manifested by an increase of the band gap, is due to a three-dimensional quantum-size effect.

II. EXPERIMENTAL PROCEDURE

A. Sample preparation

The CdSe films were deposited from an aqueous solution of $0.05M$ Na_2SeSO_3 (prepared from a stock solution of $0.1M$ black Se powder dissolved in $0.5M$ Na_2SO_3 solution), $0.04M$ $CdSO_4$, and $0.05M$ sodium nitrilotriacetate [$N(CH_2COONa)_3$ (SNTA)] as complexing agent. The pH of the solution was adjusted to between 8 and 10 with

NaOH. The exact composition of the solution is not critical, but insufficient SNTA will lead to precipitation of $Cd(OH)_2$. The use of SNTA as complexing agent is not crucial; ammonia, which is more commonly used for complexing Cd, gives qualitatively similar results. All the results shown here were obtained with SNTA.

Substrates were in most cases glass microscope slides, but Ti metal was also used when a conducting substrate was required. The cleaned substrate was immersed in the freshly-prepared solution, and left for times varying from 1 day to 1 week (depending to a large extent on the temperature of the reaction). For reactions carried out at subzero (°C) temperatures, 10–20 % methanol was added to the solution to lower the freezing point. The resulting layers were typically 200—300 nm thick. Thicker layers could be made by successive depositions. Along with film deposition, bulk precipitation of CdSe of the same color as the layers often occurred. For some experiments CdSe was electrodeposited from the same solution described above onto SnO_2-coated glass at a current density of 1–2 mA cm^{-2}.

B. Sample characterization

Optical transmission spectra were recorded between 350–850 nm. No correction was made for reflection or scattering. Reflection spectra (not shown here) showed little wavelength dependence in the region of the band gap, and this was thus ignored. Values of E_g were measured from the extrapolated intercept of $(\alpha h v)^2$ versus $h v$, where α was calculated from the transmission spectra using Beer-Lambert's law. Photoluminescence was measured under standard backscattering conditions, with exciting radiation from an argon-ion laser. X-ray powder diffraction, using Cu $K\alpha$ radiation, was carried out on both layers and precipitates. Transmission electron microscopy (TEM) and electron diffraction were carried out on layers stripped from glass substrates by dilute HCl, and floated onto grids. Elemental analyses were carried out on layers and precipitates using energy dispersive microprobe analysis, and compared to standard CdSe and CdS. Junctions were made between the CdSe and vacuum-evaporated Au (10 nm thickness) or In (20 nm) or an aqueous polysulfide solution ($4M$ K_2S $+2M$ S), and current-voltage curves were measured in the dark and under approximately AM1 illumination.

III. RESULTS

A. Optical spectra

Figure 1(a) shows the room-temperature transmission spectra of three different CdSe samples. The electrodeposited layers are dark brown in transmitted light, and if thick enough are almost opaque. The layer deposited at room temperature (20–25 °C, nominally designated as 23 °C) was orange-red in color. The layers (and precipitates) prepared at −10 °C appear orange-yellow as prepared, but deepen in color to orange at room temperature. The −10 °C spectrum in Fig. 1 was taken within a few minutes of reaching room temperature. A spectrum

taken several minutes later showed a slight shift to the red and softening of the short-wavelength knee, with little subsequent change over the next two days. Yellow layers have been prepared at −15 °C. Layers and precipitates prepared above 0 °C generally show no noticeable change in their spectra, at least over a period of weeks, at room temperature.

The square of the absorption coefficients times energy, $(\alpha h v)^2$, obtained from the spectra of the CD layers shown in Fig. 1(a), is plotted against $h v$ in Fig. 1(b) to obtain the values of band gap, assuming a direct band gap. The reasonably straight lines obtained indicate that this as-
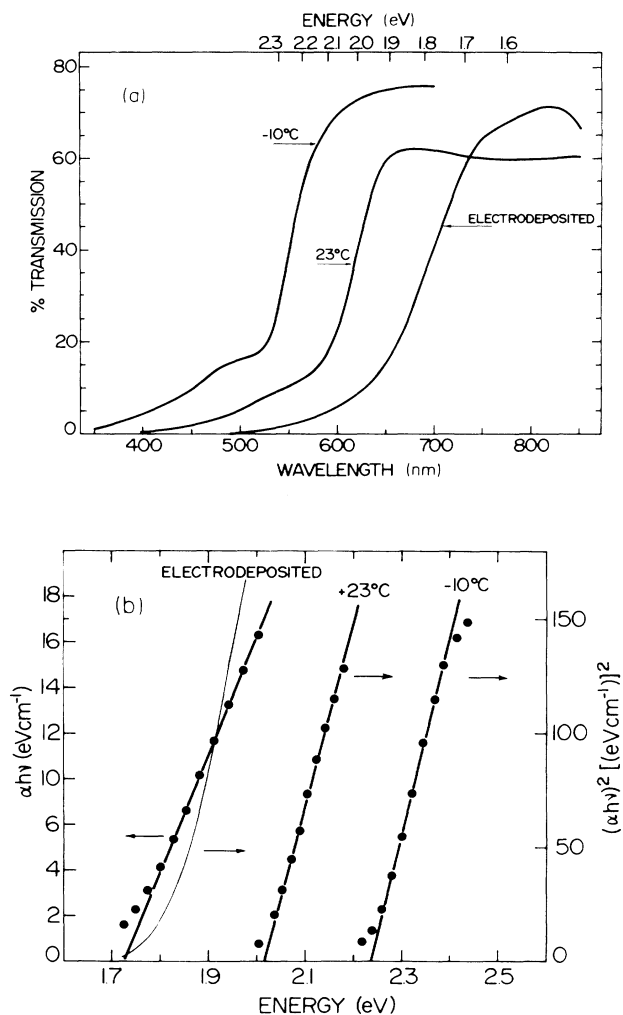

FIG. 1. (a) Optical transmission spectra of CD CdSe on glass at deposition temperatures of −10 and 23 °C (20–25 °C is room temperature). For comparison, the spectrum of a CdSe layer electrodeposited (from the same solution) on SnO_2 glass is shown. The layers are 200–300 nm thick. (b) Plots of $(\alpha h v)^n$ vs $h v$, where α was calculated from the three spectra in (a). The extrapolated intercept on the $h v$ axis gives the values of E_g for the three specimens. $n = 2$ for the CD layers and for the (thin line) electrodeposited layer, and $n = 1$ for the (thick line) electrodeposited layer.
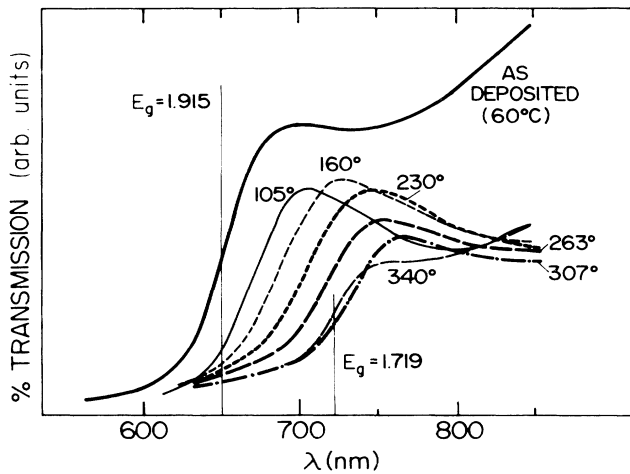
FIG. 2. Transmission spectra of a CdSe layer deposited at 60 °C and after air heating at successively higher temperatures (marked on the figure) for ~20 h at each temperature.

sumption is valid. For the electrodeposited sample, a plot of $\alpha h\nu$ versus $h\nu$ gave a better fit, with an extrapolated value of 1.726 eV for E_g. This was in agreement with the results from photoacoustic measurements. Such a linear $\alpha h\nu$ versus $h\nu$ dependence has been calculated for transitions between extended states in amorphous semiconductors.[8] We believe this deviation from the normal direct-gap behavior of CdSe to be due to local strain in the individual crystals making up the electrodeposited layers.[9]

The Cd layers darken irreversibly on heating. Figure 2 shows the spectral changes of a layer, deposited at 60 °C, as a function of annealing temperature. The two vertical lines cutting the photon energy axis indicate the values of E_g derived from the $(\alpha h\nu)^2$ versus $h\nu$ graphs of the as-deposited and 340 °C annealed layer.

B. Photoluminescence spectra

The CD CdSe layers and associated precipitates show photoluminescence which is variable in intensity from sample to sample, but often very strong and readily visible to the eye and which is blue shifted compared with single-crystal or electrodeposited CdSe. Figure 3(a), reproduced from the results of Cerdeira et al.,[10] shows photoluminescence spectra of room temperature CD CdSe, the effect of air annealing for 20 min at various temperatures, and that of a reference CdSe crystal. The photoluminescence spectrum of electrodeposited CdSe is weak and broad, but increases in intensity and sharpens after annealing, with no appreciable change in peak position which is similar to that of the single crystal. In Fig. 3(b) we show the change in E_g, measured from the peak positions of the photoluminescence spectra, as a function of annealing temperature.

C. X-ray diffraction and electron diffraction

X-ray diffraction of both layers and precipitates shows broad, weak peaks corresponding to cubic (zinc-blende)

CdSe, with no sign of preferential orientation of the layers. Peak width analyses of different samples indicate particle sizes ranging from ~35–70 Å diameter, with the lighter colored samples, prepared at lower temperatures, corresponding to the smaller sizes.

Electron diffraction of the layers also shows the CdSe to be cubic with no obvious preferential orientation. It should be noted that by itself, electron diffraction is not a definitive technique for these samples, since electron beam annealing could conceivably cause structural changes. However, in this case, the results are valid since they are in agreement with the x-ray diffraction results, this latter technique being very unlikely to cause any such change.
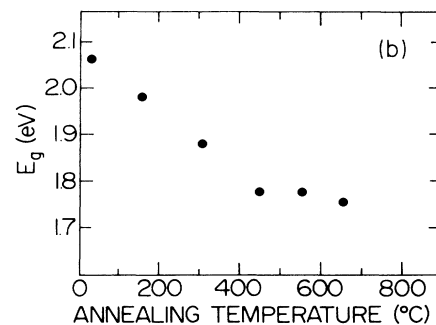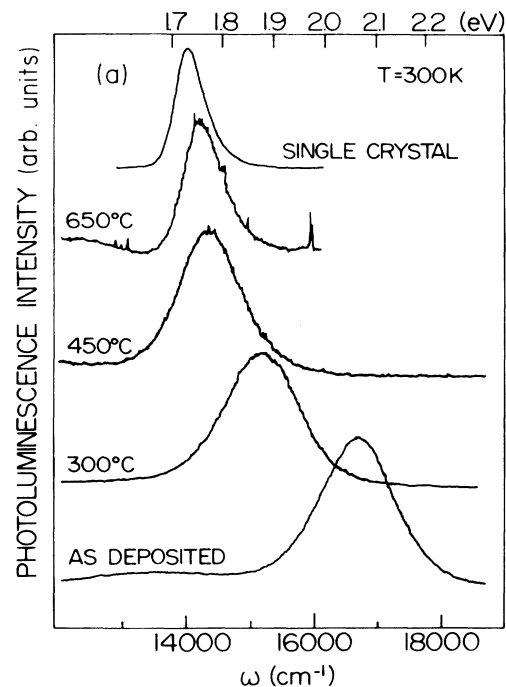

FIG. 3. (a) Photoluminescence spectra of room-temperature-deposited CdSe and after heating for 15 min at various temperatures. The spectrum of single-crystal CdSe is shown for comparison. These results are reproduced from Ref. 10. (b) Peak position of the photoluminescence spectrum of the previous CdSe sample as a function of annealing temperature.

D. Chemical analyses

Microprobe analyses of the chemically-deposited layers show the composition to be essentially CdSe, with small amounts of S (typically 3–5 % of the Se content, i.e., $CdSe_{\sim 0.96}S_{\sim 0.04}$). These small amounts of sulfur are always present in the CD layers (and absent in electrodeposited layers). They are too small to cause other than a very small increase in the band gap (~ 0.03 eV) by virtue of their effect on composition. Furthermore, heating of the samples to the point where optical and photoluminescence spectra approach those of bulk CdSe causes no change in composition, i.e., the small S content remains after such annealing.

E. Transmission electron microscopy (TEM)

Figure 4(a) shows a TEM picture of part of a room-temperature CD CdSe film. The film is clearly made up of connected small spheres or faceted particles with a typical dimension of 7 nm, although there appears to be considerable scatter in the size distribution. It is difficult to fix an upper limit, since some of the "larger" particles are obviously made up of smaller particles.

Figure 4(b) shows a lower magnification micrograph of the same sample, in which the individual particles are barely resolved. This micrograph shows how the individual small crystals are connected together in islandlike growths. The voids between the large spheres are probably due to the fact that the layers were made thin (~ 100–200 nm) for use in TEM. Scanning electron micrographs (at $\sim 1000\times$ magnification) of thicker layers show them to be essentially smooth, although considerable cracking of the layers is usual [see, e.g., Fig. 1(a) in Ref. 4, which is typical of these layers]. We note here that these layers, either on glass or on metallic substrates, are normally very cohesive, and are not visibly affected by mild mechanical treatment, such as vigorous rubbing with a cloth. Lower-temperature depositions show smaller particle dimensions. Figure 4(c) shows a high-magnification image ($270\,000\times$) of part of a layer deposited at -15 °C. In this picture, many particles of ~ 3.5 nm dimensions can be distinguished.

TEM pictures of electroplated layers show, by way of contrast, that these layers are made up of much larger single crystallites of typically 100-nm dimensions.

F. (Photo)electrical behavior

Preliminary experiments were carried out using the CD CdSe layers on Ti as the active photovoltaic absorber in metal (Au) and liquid junction (polysulfide) devices. The latter shows typical n-type behavior with dark rectifying characteristics and appreciable values of short-circuit current (SCC) and open-circuit voltage (OCV) (Fig. 5). The Au-CdSe devices (on the same CdSe layer), by way of contrast, gave very weak photovoltaic behavior, with a maximum SCC of 10 $\mu A\,cm^{-2}$. More important for the subject of the present work, they showed high-resistance, near-symmetric dark I-V characteristics as seen in Fig. 5. Values of the resistance (measured through the ~ 0.7-
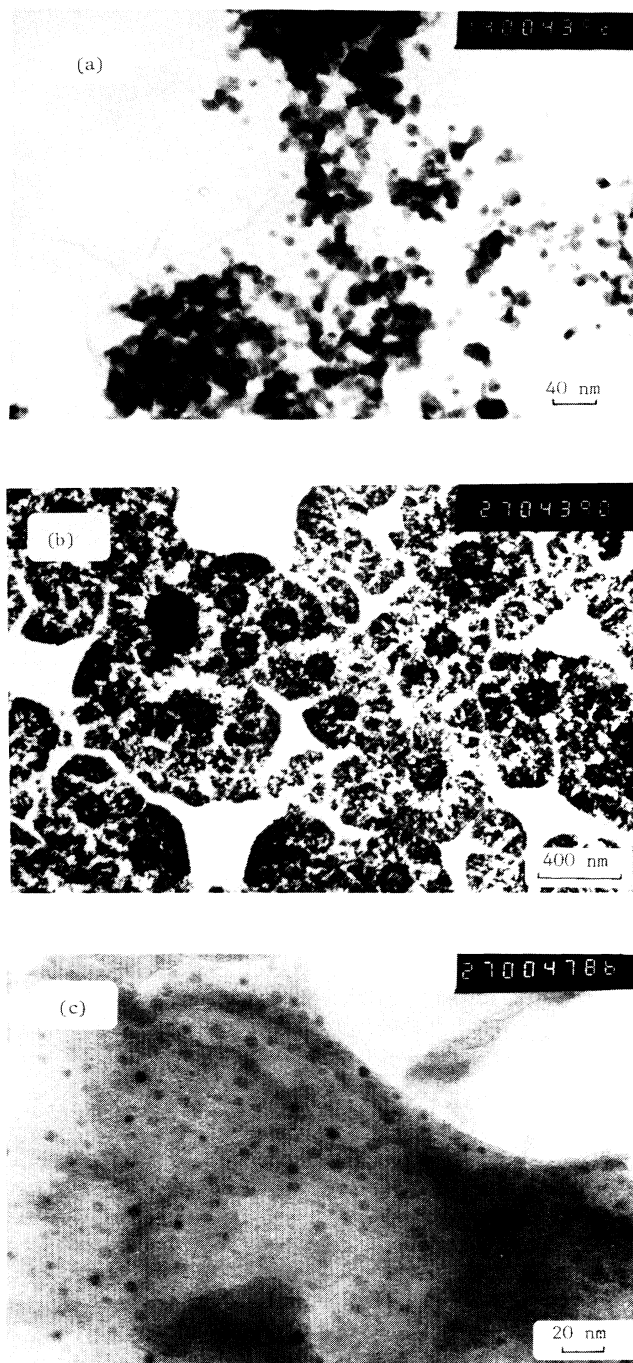

FIG. 4. (a) TEM micrograph of part of a room-temperature-deposited CdSe layer. This picture was chosen to show clearly the particle size and does not reflect the bulk structure of the layer. (b) A lower-magnification TEM picture of the above sample, to show the agglomeration of the individual particles to make up the layer. (c) TEM micrograph of a film deposited at -15 °C. The light region in the top right-hand part of the picture shows the carbon support. The darker area (rest of the picture) shows the CdSe layer, although resolution into individual particles is not evident over the entire area. For all these micrographs, the marker lines show the scale.
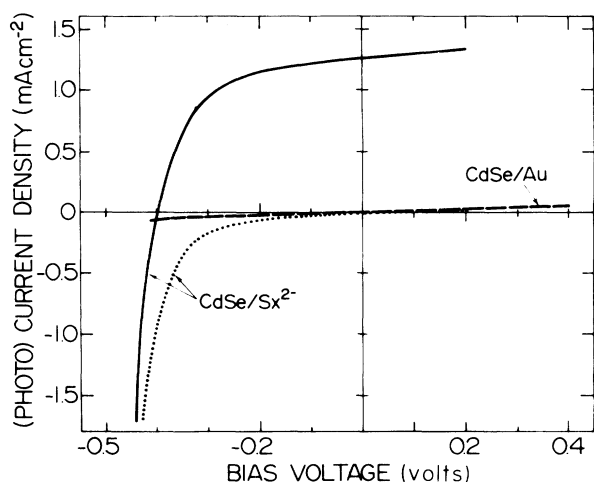
FIG. 5. Photoelectrochemical behavior (solid line, illuminated at $\sim$AM1 illumination; dotted line, dark) of a room-temperature-deposited (three successive depositions, thickness $\sim 0.7 \mu$m) CdSe layer (1 cm^2) on Ti, in an aqueous solution of $4M$ K$_2$S $+ 2M$ S. The dashed line gives the I-V behavior (on this scale, no appreciable difference between dark and illuminated behavior) of a typical 3-mm^2 Au dot (10 nm thick) evaporated on the same CdSe layer with the current adjusted to an area of 1 cm^2.

μm-thick layer), with the Ti substrate as one electrode and a 3-mm^2 Au dot as the other, were typically 1 MΩ, which is equivalent to a resistivity of $\sim 10^9$ Ω cm. Even higher values of resistance were obtained using In contacts in place of Au.

IV. DISCUSSION

The most striking visual difference between CD CdSe and normal CdSe, represented here by electrodeposited CdSe, is the change in color of the former and the range of different colors which can be prepared, as seen from Figs. 1(a) and 2. That this reflects varying direct band gaps is seen from Figs. 1(b), 2, and most convincingly, from the photoluminescence results in Fig. 3. Graphs of $(\alpha h\nu)^{1/2}$ versus $h\nu$ instead of $(\alpha h\nu)^2$ versus $h\nu$ did not lead to straight lines over any part of the optical absorption spectrum, thus supporting the interpretation of direct rather than indirect band gaps of all CD specimens measured.

The results of Kainthla et al.,[4] where they measured a band gap of 1.74 eV for their CD CdSe layers (deposited at 75 °C), would appear to be in contradiction to our results. However, their value is based on calculations made over a very narrow range of energies. Replotting their data over a wider range, towards higher energies, results in a value of ~ 1.87 eV. This agrees with that of the as-deposited layer in Fig. 2 ($E_g = 1.915$), taking into account that the latter was deposited at 60 °C, and should therefore have a slightly higher E_g than their sample.

Chemical analysis showed that the band-gap change was not due to the chemical composition, since the slight sulphur content would not explain such large shifts. Thus two possible physical explanations were considered: Either the CdSe was amorphous (or of a different crystal structure than previously known) or the layers were made up of very small, electronically isolated particles (the quantum-size effect). The results from x-ray diffraction, supported by electron diffraction measurements, which show clearly that the CdSe—both in the form of layers and precipitated powders—has the cubic zinc-blende structure, eliminated the former. The band gaps of cubic and the more common hexagonal forms of CdSe probably do not vary much. Calculation of E_g for the cubic phase has given[11] 1.9 eV at 0 K compared to ~ 1.84 eV for hexagonal CdSe.

The experiments on variation of band gap as a function of annealing temperature were carried out on the assumption that if the effect was indeed a quantum-size effect, the band gap should decrease in a more or less continuous fashion as a function of increasing temperature due to sintering of the small particles. This would lead to increasing connectivity between particles, and eventually, at high enough temperatures, to grain growth. The result in both cases is expected to be increasing delocalization of electrons; in other words, a loss in the quantum-size effect. In addition this change should be irreversible, since once particles have sintered together they will not return to their original structure when the temperature is reduced. As seen from Figs. 2 and 3, this is precisely what happens. Furthermore, the value of the band gap stabilizes at ~ 1.7 eV after prolonged annealing at ~ 300 °C., which is approximately the expected value of normal CdSe.

The most important step in confirming the validity of the quantum-size effect was to look at the microstructure of the films. The micrograph in Fig. 4(a) shows conclusively the particle nature of the layers. While there is a considerable size distribution, particle sizes of ~ 7 nm are most common for this film.

Weller et al.[1(f)] have measured the light absorption threshold (approximating the band gap) of various CdS sols and colloidal precipitates and the corresponding particle sizes, and compared the absorption threshold dependence on particle size with several theoretical models. The model which best fits the experimental results is a semiclassical approximation of the energy spectrum of a confined electron treated as an electron of reduced mass moving in the field of a sphere with a hole fixed at the center. Using this model, with both the semiclassical approximation and more accurate quantum-mechanical solution of the energy spectrum, also described by Weller et al., we can construct a graph, similar to that given for CdS by Weller et al. for CdSe, of band gap as a function of particle size (Fig. 6). A similar graph, based on the simplified formula given by Brus,[12] is also shown in Fig. 6 [curve (a)], and closely parallels the more accurate solution given by Weller et al. [curve (b)]. The semiclassical approximation [curve (c)] gives rather different results. From Figs. 1(a), 1(b), 3, and 4(a), we see that a particle size of ~ 7 nm leads to a band gap of between 2.0 and
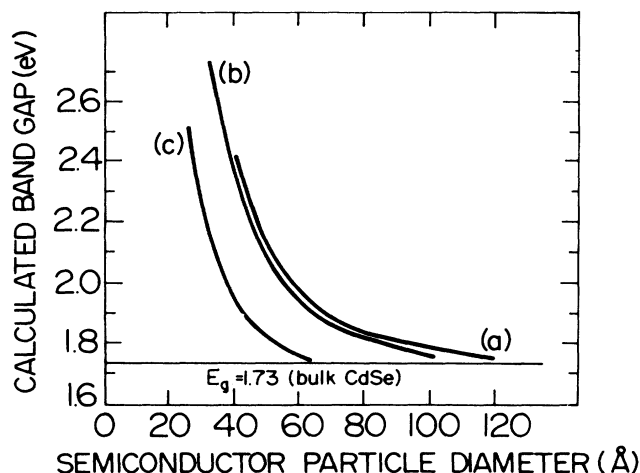
FIG. 6. Calculations from the equation given by Brus (Ref. 12) (a) and two models given by Weller et al. [Ref. 1(f)], (b) and (c) (see text), of the band gap of CdSe as a function of particle size. For these calculations, μ^*, the reduced effective mass, was taken as 0.10, and $e_{(\infty)}$, the optical dielectric constant, as 6.1.

2.1. Comparing this result with Fig. 6, we see that the more-accurate quantum-mechanical solution is closer to the experimentally observed dependence than is the semiclassical one, although still underestimating it by $\sim 30\%$. For the $-15\,°C$ deposition, with a particle size of ~ 3.5 nm, the semiclassical solution gives a band gap of ~ 2.1 eV, while the more-accurate solution, as well as the model given by Brus, give 2.6–2.7 eV. The measured value of ~ 2.3 eV (not shown in Fig. 1 for the sake of clarity, but can be reasonably extrapolated from the other results therein) falls in between those predicted by the different models. Considering the assumptions used in the model calculations, which, as pointed out by Weller et al., are not all expected to be valid, these show a fairly reasonable fit. The difference between the curves in Fig. 6, and those shown by Weller et al. for CdS (where quantum-size effects only become apparent at particle dimensions under 4 nm) is due to the lower value of reduced mass and higher value of ϵ_∞ for CdSe.

Analysis of the results up to this point shows that layers of CdSe (more accurately CdSe$_{1-x}$S$_x$ where $x \approx 0.05$) prepared by chemical deposition are made up of very small particles (typically 4–8 nm in diameter) which are physically well connected, as evidenced by the coherence and adhesion of the films, but electronically relatively isolated from each other as evidenced by the quantum-size effect which requires electron localization to the respective particles. Leaving aside for the moment the question as to why this occurs, the implications in terms of electronic device behavior should be that any solid-state device made using such layers will show a high resistance. This is borne out by the results obtained on Au/CdSe junctions (Fig. 5) which give a value for the specific resistivity of 10^8–10^9 Ω cm. There is only a very slight photovoltaic effect.

In contrast, using a liquid (polysulfide) junction, fairly reasonable photovoltaic and diode behavior is observed (Fig. 5). We believe the drastic difference to be due to the fact that a liquid can make contact throughout the bulk of the microporous film with the surface of all the individual particles. Thus if we consider photovoltaic behavior, illumination produces $e^- - h^+$ pairs in the particles. The holes can be removed by electrochemical reaction at the surface of each individual particle, leaving the particle negatively charged. The excess electron charge would create a potential gradient in the system driving the charge towards the electron sink (the substrate) presumably by interparticle hopping. For the solid junction, since no contact occurs between the Au and most of the total surface area of the CdSe, such a process will occur only to a small extent, and most of the photogenerated $e^- - h^+$ pairs will recombine without leaving their parent particle.

Returning to the transmission spectra [Fig. 1(a)], the variation of E_g with particle size can show a number of effects on the shape of the spectra. The implication of a distribution of particle sizes (and therefore values of E_g) in the same layer is that the cutoff edge should be gradual rather than sharp. The fact that a fairly sharp cutoff is obtained over a particular wavelength range suggests that one particle size is dominant. The sharpness of the curve near maximum transmission varies from one sample to another [compare $-10\,°C$ and $23\,°C$ curves in Fig. 1(a)], suggesting large variations in particle-size distribution from one sample to another. We note that the wide photoluminescence peaks (Fig. 3) can also be explained by a distribution of particle sizes.

The short-wavelength knee on the transmission curves may be a partially resolved exciton peak; the fact that this knee becomes increasingly prominent as the preparation temperature, and thus particle size, is decreased lends some support to this supposition. In one experiment a transmission spectrum of a $-15\,°C$ layer was taken at $-182\,°C$ and compared with the room-temperature spectrum. Other than a blue shift of the absorption edge by ~ 12 nm (equivalent to ~ 35 meV), no change in the shape of the knee was found, as might be expected if it was due to an excitonic transition. However, if the broad knee is connected with the size distribution of the clusters, as seems likely, such a temperature dependence might be hidden.

The shift in the spectra of the samples prepared at low temperature to longer wavelengths upon room-temperature annealing is a logical consequence of the size effect, since very small particles tend to aggregate under these conditions. The fact that the higher-temperature samples do not show this behavior to any large extent is probably more surprising.

To return to the question of why these layers are built up of small particles which are physically connected but electronically isolated, we can at present only offer some suggestions.

The mechanism of chemical deposition of CdSe is essentially based on slow release of Se^{2-} or HSe$^-$ ions (from the selenosulphate) which react with the low concentration of free Cd^{2+} (most of the Cd is complexed) to

give CdSe. The CdSe formed homogeneously throughout the solution grows into clusters which can diffuse to the substrate (and to the walls of the vessel containing the solution) where they aggregate into a layer. With time, and a high enough concentration of both Cd^{2+} and Se^{2-} (HSe^-), growth of the clusters occurs to the point where bulk precipitation occurs, hence the precipitate which often forms. That precipitation reactions can give very small particle sizes which tend to decrease with a decrease in temperature of the reaction is well known. This explains our observation that the band-gap shift of the layers increases with decreasing deposition temperature.

The electronic isolation between particles implies a potential barrier between them. A surface potential barrier could arise due to the presence of a surface insulating layer such as appears to occur in the precipitates of Fojtik et al.[2] Preliminary x-ray photoelectron spectroscopy (XPS) analyses do not show the surface to be anything other than CdSe (with the usual surface oxygen and carbon appearing in the spectrum). However, it is conceivable that the surface contains a considerable amount of oxide (or hydroxide) which we could not identify in our XPS results.

The normal intergrain potential barrier between crystallites in a polycrystalline material, resulting from a space-charge layer in the crystallites, is less likely to be operative here. This is because the dimensions of the particles excludes the existence of an appreciable space-charge layer in the individual particles for all but very highly doped material.

The small but ever-present amount of sulfur in the CdSe comes from the selenosulfate, but we cannot at present say whether or not it plays a role in determining the properties of the CdSe.

In conclusion, we have shown that chemically deposited CdSe films show a variable increase in band gap which is due to the very small particle structure of the films, causing a quantum-size effect. This is the first time where the three-dimensional quantum effect has been shown to occur in a coherent film. The existence of this effect in a thin film, as contrasted with colloids and precipitates, has a number of implications. Of particular note is the possibility of direct electrochemical potential and current measurements of (photo)electrochemical reactions on small semiconductor particles.

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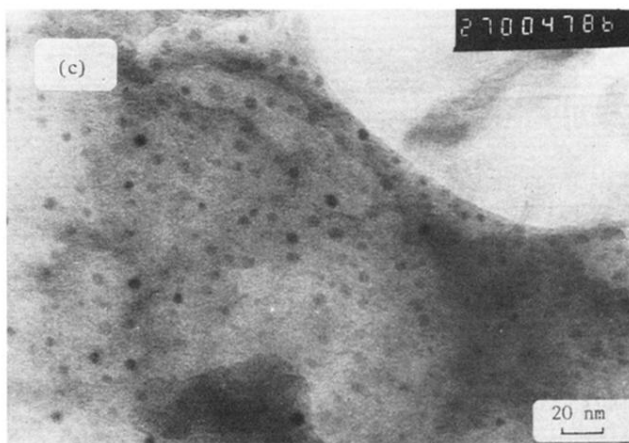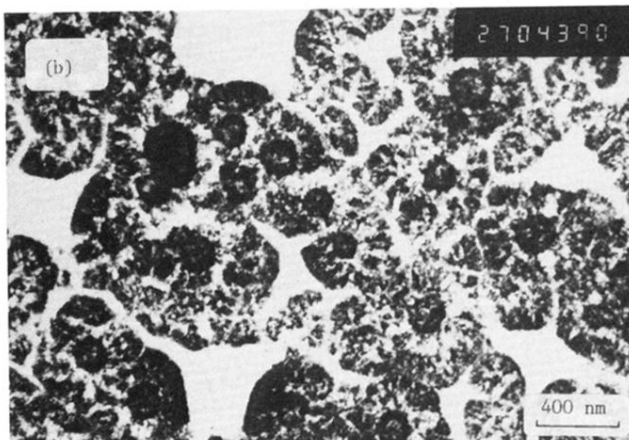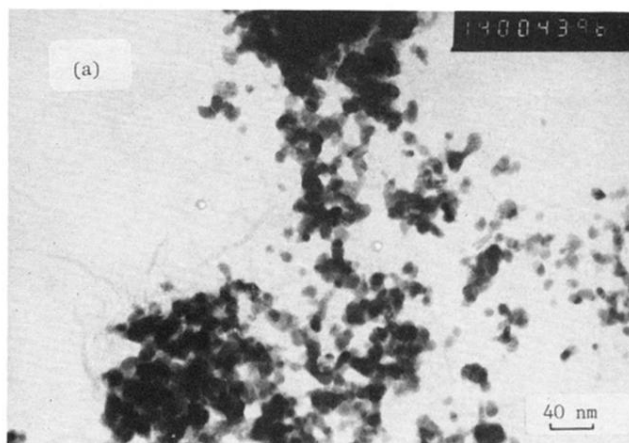[12]L. Brus, J. Phys. Chem. **90**, 2555 (1986).

FIG. 4. (a) TEM micrograph of part of a room-temperature-deposited CdSe layer. This picture was chosen to show clearly the particle size and does not reflect the bulk structure of the layer. (b) A lower-magnification TEM picture of the above sample, to show the agglomeration of the individual particles to make up the layer. (c) TEM micrograph of a film deposited at −15 °C. The light region in the top right-hand part of the picture shows the carbon support. The darker area (rest of the picture) shows the CdSe layer, although resolution into individual particles is not evident over the entire area. For all these micrographs, the marker lines show the scale.