Charge transport in CdSe nanocrystalline sublayers of SiO_x/CdSe multilayers and composite SiO_x-CdSe thin films

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Abstract. Dark-current measurements have been carried out on SiO$_x$/CdSe multilayers and composite SiO$_x$–CdSe thin films having varying CdSe sublayer thicknesses and average nanocrystal sizes and, for comparison, on SiO$_x$ and CdSe single layers. Size-induced changes in room temperature conductivity and dark-current activation energy at temperatures $T > 320$ K have been observed in both multilayers and composite films. The high-resolution electron microscopy studies performed have shown that: (i) the CdSe sublayers in the multilayers are nanocrystalline with nanocrystallite size equal to the sublayer thickness; and (ii) the CdSe nanocrystals in the composite films are disposed in SiO$_x$–CdSe 'sublayers' having high CdSe volume fractions. The conclusion has been reached that in both multilayers and composite films charge transport, in the layer plane, involves networks of CdSe nanocrystals contacting each other. It has been found that in the SiO$_x$/CdSe multilayers charge transport is controlled by potential barriers for electrons existing at the CdSe nanocrystal interface and that the barrier height does not exceed 0.25 eV. In the SiO$_x$–CdSe composite films the potential barriers at the CdSe–CdSe interface do not appreciably affect the charge transport, due to the great conductivity increase, induced by the SiO$_x$ matrix. The observed size-induced changes in the dark conductivity and dark-current activation energy in these films have been attributed to an upward quantum-size shift of the conduction band bottom in CdSe nanocrystals.

1. Introduction

Non-linear optical properties of semiconductor-doped glasses [1–3] and radiative recombination in various semiconductor nanocrystals (NCs) [4, 5] have been the subjects of extensive studies during the last fifteen years. However, the investigation of these materials in connection with their technologically important transport-related applications, in particular transport mechanisms, has received relatively little attention [6–9]. Besides this, due to the great diversity of systems comprising semiconductor NCs, various charge-transport mechanisms have been suggested [6, 8–10]. In thin films of silicon NCs [9], dark-carrier transport has been related to a conduction mechanism, encompassing both geometric and electronic effects. In accordance with percolation theory, the films have been modelled by a network of resistors, the carriers following the path of least resistance through the film (formed by large particles). Space-charge-limited currents have been observed at high applied fields. In the case of Si-rich SiO$_2$ thin films deposited on c-Si substrates [6], in which the excess atomic Si forms silicon nanoclusters with volume fraction below the percolation threshold, a Fowler–Nordheim

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tunnelling of electrons in Si nanoclusters through the SiO_2 barriers has been assumed. Finally, for composites of semiconductor NC/carrier-transporting polymer [8, 10] it has been concluded that NCs are not directly involved in carrier transport; the polymer matrix is responsible for charge transport while the presence of semiconductor NCs enhances the efficiency of the photoinduced charge generation and extends the sensitivity range.

In this article, charge transport in two kinds of sample from the system SiO_x–CdSe: multilayers of SiO_x/nanocrystalline CdSe and composite SiO_x–CdSe thin films, has been studied by measuring the temperature dependencies of the dark current. Size-induced changes in the room temperature conductivity and dark-current activation energy have been investigated. Fairly different charge-accumulation effects of SiO_x on CdSe NCs have been observed in multi-layers and composite films. The transport mechanisms for both groups of samples have been discussed in terms of the model developed for polycrystalline semiconductors.

2. Experimental details

Two groups of samples were investigated: (I) multilayers (MLs) of SiO_x/CdSe having CdSe sublayer thicknesses $d_w = 2.5, 3.0, 3.5, 4.0, 5.0$ and 10.0 nm; and (II) thin composite films of SiO_x doped with CdSe NCs with average nanocrystal diameters $d = 3.0, 4.0, 5.0$ and 7.0 nm. The average NC size was determined by means of x-ray diffraction and high-resolution electron microscopy (HREM) measurement [11].

All samples were fabricated as 'sublayers' from SiO_x and CdSe deposited successively on Corning 7059 glass substrates by thermal evaporation of powdered CdSe (Merck, 'Suprapure') and granular SiO from two independent tantalum crucibles in a vacuum of $\sim 10^{-3}$ Pa [12, 13]. During the preparation procedure, the substrates were maintained at room temperature. They were rotated at a rate varying between 8 and 30 turns min^{-1} when CdSe 'sublayers' of all samples and SiO_x sublayers of MLs were deposited. When SiO_x–CdSe composite films were fabricated, the SiO_x matrix 'sublayers' were deposited with substrates fixed above the SiO_x crucible. The film thickness and deposition rate, for both materials, were controlled during deposition by two previously calibrated quartz monitors, MIKI-FFV, whose quartz crystal heads were fixed above the respective crucibles. The ratio of SiO_x to CdSe 'sublayer' thickness was kept constant in each group of samples, being 1.3 and 20 for the first and second group respectively. The total number of sublayer pairs was varied between 15 and 60 depending on the sublayer thickness. In order to ensure that the composition of the SiO_x was the same ($x \approx 1.5$ [12]) for all samples, the rate of deposition SiO_x was kept constant (~ 3.5 nm s^{-1}). All samples studied were annealed in air for 90 min at 670 K.

Planar contacts (about 1 cm long and 0.1 cm apart) were used for the dark-current and photocurrent temperature measurements carried out in the direction parallel to the layer plane. In–Ga alloy was used for the SiO_x/CdSe MLs and evaporated aluminium (or sputtered silver) for the SiO_x–CdSe composite films. In order to ensure access of the contact material to all sublayers, the samples were initially scratched by a stainless steel pin. The current–voltage characteristics measured were linear for the fields applied ($\lesssim 10^3$ V cm^{-1}). During the measurements, the samples were heated at a rate of 0.05 K s^{-1}.

3. Results and discussion

3.1. Charge transport in CdSe nanocrystalline sublayers of SiO$_x$/CdSe MLs

Dark-current temperature dependencies measured for SiO_x/CdSe MLs with various sublayer thicknesses are shown in figure 1. The dark-current activation energy E_{ad} was determined for
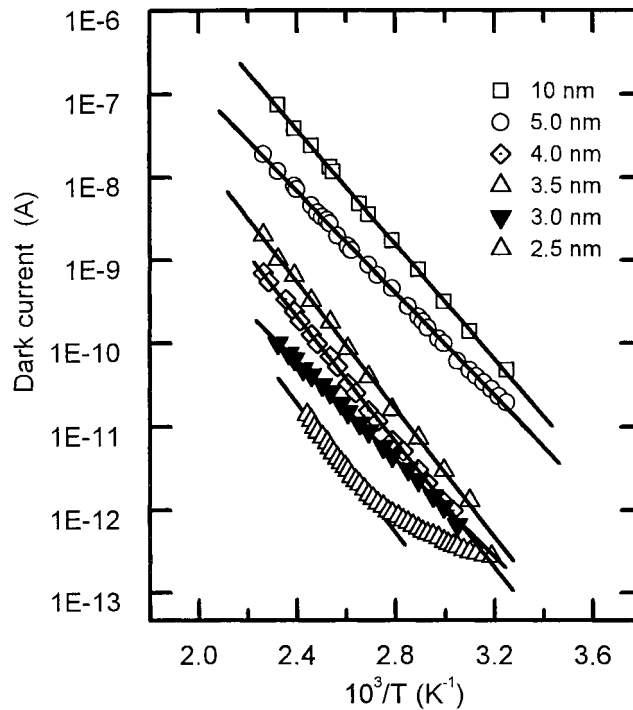
Figure 1. Dark-current temperature dependencies of SiO_x/CdSe multilayers having various sub-layer thicknesses and a total thickness of about 0.2 μm. The measurements were carried out under applied fields of 5×10^2–10^3 V cm^{-1}. Each set of symbols represents current values measured on a ML with the CdSe sublayer thickness given in the figure. The respective solid lines correspond to fits of the experimental results made in accordance with the relation $I_d = I_{d0} \exp(-E_{ad}/kT)$ (see the text for details).

all samples from the slope of the high-temperature part of the curves in accordance with the relation $I_d = I_{d0} \exp(-E_{ad}/kT)$, where k is the Boltzmann constant and T the temperature. The values $\sigma_d \approx 5 \times 10^{-12}$ S cm^{-1} and $E_{ad} = 0.55$ eV were determined for the room temperature conductivity and dark-current activation energy (at $T > 300$ K) of the SiO_x ($x \approx 1.5$) single layers. Polycrystalline CdSe single layers (made under the same preparation conditions as the CdSe sublayers) having thickness of 200 nm have also been studied and the values $\sigma_d \approx 5 \times 10^{-7}$ S cm^{-1} and $E_{ad} = 0.55$ eV have been obtained. In both materials the major charge carriers are the electrons. Our previous studies on resonant Raman scattering and photoluminescence from SiO_x/CdSe MLs have indicated [14] that, along the ML axis, electrons in CdSe are not confined while the holes should be confined in potential wells having depths of about 1.3 eV. Besides this, the extremely low ($\sim 4 \times 10^{-9}$ cm^2 V^{-1} s^{-1}) electron mobility in thermally evaporated SiO_x films [15] and the much higher one (>100 cm^2 V^{-1} s^{-1}) in polycrystalline CdSe layers [16] imply that charge transport in the direction parallel to the layer plane should be along CdSe sublayers. The values of σ_d (calculated assuming charge transport via CdSe sublayers only) and E_{ad} (henceforth related to the CdSe sublayers) obtained for the ML samples are shown in table 1. It is seen that E_{ad} exhibits a non-monotonic change with sublayer thickness; however, for all MLs, it remains higher than that of CdSe single layers. The ML conductivity is considerably lower (10^2–10^3 times) than that of CdSe single layers and it decreases with sublayer thickness. However, it remains 10–500 times higher than

Table 1. Experimental parameters of SiO$_x$ and CdSe single layers and SiO$_x$/CdSe multilayers manufactured in the same way.

CdSe sublayer thickness, d_w (nm)	Annealing time (min)	Dark conductivity, σ_d (S cm^{-1})	Dark-current activation energy, E_{ad} (eV)	Photocurrent-to-dark-current ratio I_p/I_d	Photocurrent activation energy, E_{ap} (eV)
SiO$_x$ (200 nm)	60	5×10^{-12}	0.55	—	—
CdSe (200 nm)	60	5×10^{-7}	0.55	1×10^3	0.12
10.0	60	2.5×10^{-9}	0.68	5×10^3	0.13
5.0	60	1×10^{-9}	0.62	2×10^4	< 0.1
4.0	120	8×10^{-11}	0.80	3×10^3	0.23
3.5	60	5×10^{-11}	0.77	2×10^3	0.13
3.0	60	1×10^{-10}	0.63	1×10^3	—
2.5	90	5×10^{-11}	0.83	1×10^3	0.23

the conductivity of the SiO$_x$ single layers, which supports the above assumption that charge transport in the ML plane passes through the CdSe sublayers.

For nanocrystalline silicon films [9], because of the observed weak temperature dependence of the dark conductivity, it has been suggested that carrier transfer from one particle to the next is realized either by tunnelling through energetic barriers between NCs or by space-charge-limited currents. It has been shown [11] that CdSe sublayers of MLs are nanocrystalline with average NC size approximately equal to the sublayer thickness. The CdSe NCs are randomly oriented, which may induce a great number of defects at the CdSe–CdSe interfaces. On the other hand, the sample annealing in air may also affect NC surfaces by producing either physical or chemical oxygen absorption [17]. One may expect, as for II–VI microcrystalline films [18], interface defects to cause upward bending of the conduction band of CdSe NCs and, thus, potential barriers for electrons to exist at CdSe–CdSe NC interfaces. However, for SiO$_x$/CdSe MLs a strong thermal dependence of the ML dark conductivity and linear current–voltage characteristics have been observed. These results differ from those reported for nanocrystalline silicon films [9] and give us a basis for assuming that in CdSe nanocrystalline sublayers, charge transport can be described using the model developed for polycrystalline semiconductors. In the framework of this model, the observed decrease of ML conductivity with decreasing sublayer thickness may be related to the increase of interface-to-volume ratio for CdSe NCs. According to the model [18], the dark-current activation energy in MLs should be a sum of the Fermi energy E_F in CdSe NCs and the height of the interface potential barriers E_b, i.e. $E_{ad} = E_F + E_b$. The upward bending of the conduction band causes a gradual increase in E_F as the CdSe NC size decreases and, for this reason, the E_{ad}-values measured for MLs are higher than those of the CdSe single layers (table 1). The non-monotonic E_{ad}-change observed may be assigned to some fluctuations in the barrier height connected with either different duration of the annealing procedure (table 1) or some other uncontrolled variations in the preparation conditions.

In order to obtain information about the heights of the interface barriers in SiO$_x$/CdSe MLs, we have measured temperature dependencies of the photocurrent (under white-light illumination and for $T > 290$ K). Photocurrent activation energies E_{ap} determined from these dependencies are shown in the last column of table 1. One can see that, in general, the higher the dark-current activation energy, the higher the photocurrent activation energy of the sample. It is known that photocurrent in polycrystalline films may be described [18] by the relation $I_p = I_{p0} \exp(-E_{ap}/kT) \sim \mu_D \tau$, where $\mu_D = \mu_{D0} \exp(-E_b/kT)$ is the carrier drift mobility and τ is the carrier lifetime. Moreover, in disordered semiconductors [19] the temperature
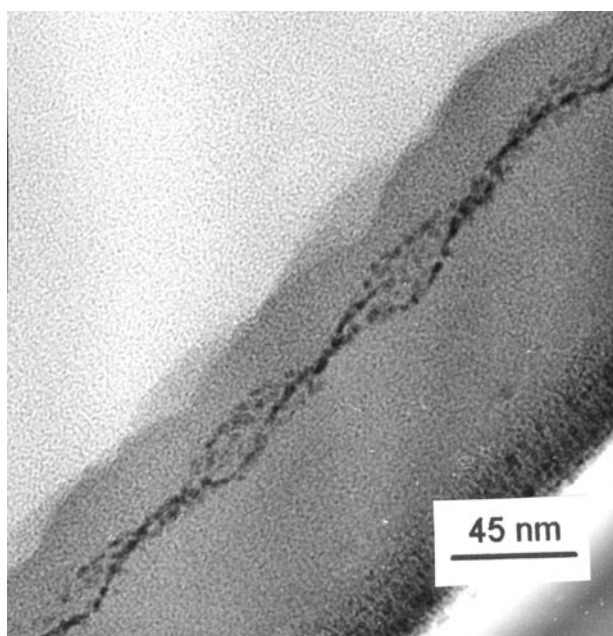
dependence of the carrier lifetime is much weaker than that of the drift mobility, and thus $E_{ap} \approx E_b$. The observed similarity of the changes in E_{ap} (E_b) and E_{ad} supports the above assumption that some variations in the barrier height are responsible for the E_{ad}-variations in the MLs and indicates that the E_b-value should not exceed 0.25 eV. Thus, significant three-dimensional electron and phonon confinement in CdSe NCs could not be expected, which is in conformity with the conclusion already reached on the basis of the resonant Raman scattering and photoluminescence studies carried out on SiO_x/CdSe MLs [14].

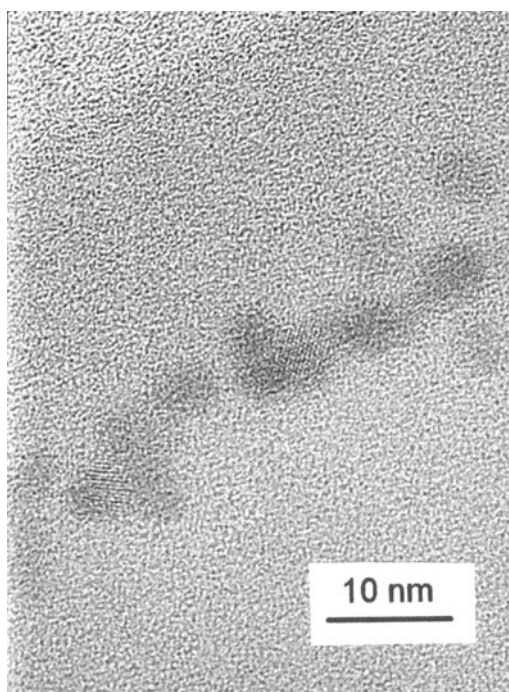### 3.2. *Charge transport in SiO_x–CdSe composite films*

Activation energies determined from the dark-current temperature dependencies of SiO_x–CdSe composite films at $T > 320$ K and applied fields $F < 10^3$ V^{-1} cm^{-1} are given in table 2. It is seen that in the films with large CdSe NCs, the dark-current activation energy (0.4 eV) is smaller than the value of 0.55 eV obtained for SiO_x and CdSe single layers; it increases with decreasing NC size. Room temperature conductivity could be calculated assuming that the dark current goes through the total thickness of the composite films. However, because of the extremely low electron mobility in thermally evaporated SiO_x films [15] and the much higher electron mobility in polycrystalline CdSe [16], it is not quite possible for electron transport in the direction parallel to the 'sublayer' plane to go through the full cross section of the films. Cross sectional electron micrographs of a SiO_x–CdSe composite film (obtained at two different magnifications with a JEM 400 EX microscope operating at 400 kV) are shown in figures 2(a) and 2(b). Figure 2(a) shows that because of the specific preparation technique used [12], CdSe NCs are situated in 'composite sublayers' having high CdSe volume fractions (above the charge percolation level). 'Sublayers' of 'pure' SiO_x separate them, as they are more than ten times thicker than the composite ones. For such a CdSe NC configuration, it seems reasonable to assume that charge transport goes mainly through the SiO_x–CdSe 'composite sublayers'. This assumption was verified by dark-current measurements carried out in the direction perpendicular to the layer plane of SiO_x–CdSe films, deposited on polished aluminium substrates. In this case, carrier transport crosses the thick SiO_x 'sublayers' and, as had been expected, the ratio of parallel to perpendicular conductivity measured was $>10^2$. That is why the average dark conductivity of the SiO_x–CdSe composite films given in table 2 has been calculated adopting the convention that electron transport goes only through the 'composite sublayers'. One can see that the conductivity of the 'composite sublayers' having large (5 and 7 nm) NCs is much higher than that of the CdSe polycrystalline single layers ($\sim 5 \times 10^{-7}$ S^{-1} cm) and decreases with decreasing average NC size. Nevertheless, the conductivity of 'composite sublayers' with 4 nm NCs is significantly higher than that of the

Table 2. Experimental parameters for SiO_x and CdSe single layers and SiO_x–CdSe composite films manufactured in the same way.

Average CdSe NC diameter, d (nm)	SiO_x total thickness (μm)	Dark conductivity, σ_d (S cm^{-1})	Dark-current activation energy, E_{ad} (eV)
SiO_x (1.0 μm)	1.0	5×10^{-12}	0.55
CdSe (200 nm)	0.2	5×10^{-7}	0.55
7.0	1.92	2×10^{-4}	0.40
5.0	1.28	2×10^{-4}	0.40
4.0	1.24	3×10^{-7}	0.50
3.0	1.46	1×10^{-9}	0.87

(a)

(b)

Figure 2. Cross sectional electron micrographs of a SiO$_x$–CdSe composite film, obtained at two different magnifications: (a) 110 000 times; the formation of a CdSe 'composite sublayer' is clearly seen; (b) 500 000 times; it is seen that because of the high volume fraction of CdSe in the 'composite sublayer', some of the nanocrystals contact each other.

CdSe nanocrystalline sublayers of SiO$_x$/(4 nm)CdSe MLs and becomes almost equal in the case of 3 nm NCs in both kinds of sample.

It is clear from figure 2(b) that some CdSe nanocrystals are isolated while some of them contact each other. This implies that, most probably, CdSe nanocrystals are directly involved in carrier transport. In accordance with percolation theory, a network of NCs forms, for electrons, the path of least resistance through the 'composite sublayers'. The observed strong dark-current temperature dependence indicates that the approach applied to the charge transport in the SiO$_x$/CdSe MLs may be used for the SiO$_x$–CdSe composite films as well. It is interesting that, though the NC network in the 'composite sublayers' is not so densely packed as that in CdSe nanocrystalline sublayers of MLs, their conductivity is quite high.

It was reported [20, 21] that the thermal evaporation of a SiO$_x$ layer onto a CdSe film may produce an accumulation layer at the SiO$_x$–CdSe interface, thus causing a Fermi-level shift upwards in the interface region of the CdSe film. It was also found [21] that, in the accumulation layer, the room temperature conductivity is more than a hundred times higher than that in the bulk of the film. Since CdSe NCs embedded in a SiO$_x$ matrix are very small, it may be suggested that the SiO$_x$ induced accumulation layer occupies the entire volume of each CdSe NC. Moreover, the low E_{ad}-values measured for the large NCs imply that, due to the accumulation effect of SiO$_x$, the potential barriers for electrons at the CdSe NC contact interfaces should be very low, i.e. $E_{ad} = E_F + E_b \approx E_F$. On the other hand, a size-induced increase in the optical band gap of CdSe NCs has been observed [12, 22] in SiO$_x$–CdSe composite films and related to quantum-size upward shift of the CdSe conduction band bottom. This means that, at a fixed Fermi-level position, the dark-current activation energy in NCs should increase with decreasing NC size. It seems that in samples having CdSe NCs of 5 and 7 nm, the upward shift of the Fermi level, which is due to the accumulation effect of SiO$_x$, is the dominant effect. The observed conductivity decrease and E_{ad}-increase on decreasing the NC size to below 5 nm (table 2) is, most probably, due to a great size-induced upward shift of the conduction band bottom, not compensated by the accumulation effect of the SiO$_x$ matrix.

Now, we return to the above-mentioned peculiarity that dark conductivity measured in SiO$_x$/CdSe MLs is considerably lower than that of the respective composite films having CdSe NCs of the same average size (compare table 1 and table 2). It has been observed [20] that the thinner the SiO$_x$ layer deposited on the CdSe film, the weaker the accumulation effect in the CdSe interface region. Bearing this result in mind, we assume that the very thin (2.5–10 nm) SiO$_x$ sublayers of SiO$_x$/CdSe MLs have no accumulation effect on the CdSe sublayers, while the much thicker (20–100 nm) SiO$_x$ 'sublayers' in the SiO$_x$–CdSe composite films strongly affect the CdSe NC conductivity. This result is very interesting from a practical point of view. It makes it possible to achieve considerable variations in the dark conductivity and photoconductivity of CdSe NCs by varying just the thickness of the SiO$_x$ sublayers of SiO$_x$/CdSe MLs and SiO$_x$–CdSe composite films.

4. Conclusions

Room temperature conductivity and dark-current activation energy have been measured in order to study charge transport in SiO$_x$/CdSe multilayers and SiO$_x$–CdSe composite films in the direction parallel to the layer plane. A comparison has been made with the dark conductivity and activation energy of SiO$_x$ and CdSe single layers as well as with the conductivity of the composite films in the direction perpendicular to the plane. It has been concluded that for both groups of samples the charge transport goes through a network of CdSe nanocrystals formed in each CdSe sublayer of the SiO$_x$/CdSe multilayers or SiO$_x$–CdSe 'sublayer' of the composite

films. The existence of such NC networks in the composite films has been confirmed with HREM studies. It has also been found that the potential barriers for electrons at CdSe–CdSe NC interfaces, whose height does not exceed 0.25 eV, play an important role in charge transport via nanocrystalline CdSe sublayers of SiO_x/CdSe MLs while, in the case of composite films, their role is marginal.

The great NC conductivity observed in SiO_x–CdSe composite films has been related to electron transfer from the SiO_x matrix to the CdSe NCs. This transfer induces a significant Fermi-level shift of the NC conduction band bottom, which exceeds the size-induced conduction band upward shift in the big (5–7 nm) CdSe NCs and partially compensates for it in the small NCs. Such electron transfer has not been observed in MLs, which has been connected with the very small thickness of SiO_x sublayers. Thus, we have found a practical way to vary the CdSe NC conductivity, by varying the SiO_x sublayer thickness in the SiO_x–CdSe system.

Acknowledgments

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