Tripathi, T. S.; Terasaki, I.; Karppinen, M.

Anomalous thickness-dependent optical energy gap of ALD-grown ultra-thin CuO films

Published in:
Journal of physics: Condensed matter

DOI:
10.1088/0953-8984/28/47/475801

Published: 16/09/2016

Please cite the original version:
Introduction

Materials of reduced dimensionality often surprise our conventional wisdom when the dimensions are below some characteristic length scales of the material through the phenomena called quantum size effects [1,2]. It is a well-proven fact that in normal semiconductors when the crystallites radius is less than or comparable to the Bohr excitonic radius,

\[ r_B = \frac{4\pi\varepsilon_0\varepsilon_r\hbar^2}{e^2\left(\frac{1}{m_e} + \frac{1}{m_h}\right)} \quad (1) \]

electrical and optical properties of the material get significantly affected by the quantum size effects [3,4]; here \( \hbar = \hbar/(2\pi) \), \( \hbar \) is the Planck’s constant, \( m_e/m_h \) is the effective mass of electron/hole (often being only a small fraction of the electron mass [5]), \( e \) is the electron charge, \( \varepsilon_0 \) is the permittivity of free space or vacuum and \( \varepsilon_r \) is the relative dielectric constant of the semiconductor. Generally, the thickness of thin films changes proportionally with the grain or crystallite size, and often an inverse square dependence of the optical energy gap on the film thickness is reported in literature due to dominant quantum localization effects [6]. However, in the small-size regime, microstructural features such as dislocations, crystal defects, surface states and electron-hole Coulombic attractions may result in different dependences depending on the dominant interactions [7,8]. Usually, Coulomb attractions among charge carriers are ignored or considered less important to the overall optical energy gap shift due to the dielectric screening effect of the material.

The first attempt to understand the increase in optical energy gap in semiconducting materials with crystallites radii in the few-nanometer range was based on the effective mass approximation and neglected the Coulomb attractions between the spatially confined electrons and holes [9]. Brus [10,11] was then the first to consider the Coulombic attraction between the electrons and holes confined within the nanocrystals. Within the effective mass approximation he formulated an exciton (bound state of an electron and a hole) like Hamiltonian for the crystallite excited state, i.e.,

\[ \hat{H} = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_h}\nabla_h^2 - V_0(r_e, r_h) \quad (2) \]

Here \( V_0 \) is the potential energy outside the crystallite surface and \( r_e \) and \( r_h \) are the electron and hole positions within the crystallite. When \( V_0 \) is infinite this Hamiltonian turns into a hydrogen atom like Hamiltonian, resulting in energy values slightly below the optical energy gap [12,13]. The small effective masses of electrons and holes in the above Hamiltonian result in strong localization or large kinetic energy of electrons and holes in comparison to the Coulomb attraction. Moreover, the Coulomb attraction gets screened due to the large dielectric constants of inorganic semiconductors, being typically in the range of 5 to 12. Consequently the optical energy gap decreases as the crystallite radius increases. In other words, exciton wave functions extend over a large space of the material. However, in the case of small crystallites the bulk energy level scheme may not be valid as the Coulomb attraction between spatially confined electrons and holes in nanometer range is more pronounced and the crystallites size effects may create a qualitatively different situation.

In his calculations leading to the “effective mass approximation model”, Brus [14,15] showed that the Coulomb attraction in the case of spatially confined charge carriers within a semiconductor nanocrystal cannot be neglected. Even though his work is the most anticipated in
describing the quantum confinement effects in nanocrystalline materials, it fails to provide a quantitatively good agreement with the experimental data for the smallest nanocrystals. As the possible explanations the following points have been raised: (i) the energy surfaces of the parabolic form (such an approximation is valid near k = 0, i.e., near the center of the Brillouin zone but not in the entire k-space), (ii) the bulk relative dielectric constants of the materials for Coulomb energy calculations, (iii) the infinitely large potential outside the spherical nanocrystal within which the electrons and holes are confined. Several improvements have been made since then to provide a better overall quantitative agreement with the experimental data, e.g., a hyperbolic band model with non-parabolic electron and hole bands [16], and the finite height of the potential energy outside the nanocrystal-surrounding interface [17]. The basic physics of quantum confinement, though, is understood in the light of the Brus model; nevertheless there is definitely space for new experimental data for the deeper understanding. For instance, the models so far proposed are for direct optical energy gap materials and the possibly different situations in the case of an indirect band are not known. The relative dielectric constant of the materials has been considered constant (usually the bulk value \( \varepsilon_{r,\infty} \) or the bulk static value \( \varepsilon_{r,s} \) is taken) for the calculation of the Coulomb attractions whereas strong indications are there in the exciton literature that the dielectric screening should get significantly reduced in the nanometer regime for semiconductor nanocrystals [13]. Having understood all this, here in this manuscript we report on the decrease of the optical energy gap with decreasing film thickness for ultrathin films of CuO in the thickness range of 9–81 nm fabricated using the state-of-the-art thin film technique, i.e., atomic layer deposition (ALD). We attempt to understand the unusual dependence in the light of “effective relative dielectric constant” as proposed in Ref. 18.

Copper oxide exists mainly in three distinct stable binary oxide phases, namely Cu2O, Cu3O4 and CuO. Among these three phases, Cu2O has been most intensely investigated in the past both experimentally [19,20,21] and theoretically [22,23,24] for its applicability in optoelectronics and solar cell technologies. It is naturally a p-type semiconductor with an optical energy gap of 2.1 eV. However, there are several issues as summarized in the review by Rai [25] that limit the use of Cu2O in solar cell applications. With the apparent new interest in copper oxides for their potential application in next-generation sustainable energy technologies based on earth-abundant elements/materials, optical and electronic properties of the other two copper oxide phases are now gaining increasing attention as well. The divalent copper oxide CuO is often referred to as a narrow-gap semiconductor with an optical energy gap of 1.2-1.9 eV [26,27,28]. However, several experimental reports concerning both the type (direct [29] or indirect [30,31,32,33]) and the width of the optical energy gap are inconclusive; for the optical energy gap the reported values vary from 1.3 to 2.1 eV [34,35,36,37]. In their recent review, Meyer et al. [35] discussed the current status of semiconducting copper oxide thin films and demonstrated that CuO and Cu3O5 thin films have optical energy gap energies roughly in the most attractive range of 1–2 eV. There are very few reports about the dependence of the optical energy gap on the thickness of CuO thin films. Very recently, Akaltun [38] reported the decrease of the optical energy gap with increasing film thickness for CuO thin films prepared by the successive ionic layer adsorption and reaction (SILAR) technique. However, the films were quite thick (>200 nm) and may therefore necessarily not be compared to the results reported in this manuscript. Moreover, there are few reports for CuO nanoparticles where a proportional dependence between the optical energy gap and the nanocrystallites diameter has been observed due to the defect states within the optical gap. [39,40]

The ALD thin film technique employed here is based on self-limiting surface-saturative reactions of alternately pulsed gaseous precursors. This unique deposition mechanism allows for the excellent thickness control for homogeneous and pinhole-free thin films deposited on high aspect ratio geometries [41,42]. Copper oxides (CuO and Cu3O4) have previously been deposited on various surfaces and geometries via ALD using several copper precursor/oxygen source combinations [43,44,45,46]. In a majority of these works, the main objective was to produce pure metallic copper films through reduction of the as-deposited copper oxide film. Our interest in the CuO films stems from the goal to find compatible p-type electrode materials for thin-film thermoelectrics, transparent electronics and solar cell modules [47,48,49,50].

**Experimental**

Our CuO thin films were deposited from copper 2,2,6,6-tetramethyl-3,5-heptanedionato (Cu(thd)2) as the source for copper and ozone as an oxygen source in a commercial hot-wall flow-type F-120 ALD reactor (ASM Microchemistry Ltd., Finland) operated under a nitrogen pressure of 2–3 mbar. The films were deposited on 3.5x3.5 cm2 borosilicate substrates. The as-deposited films were crystalline, but to enhance the crystallinity, a post-deposition heat treatment was carried out at 400 °C in a rapid-thermal-annealing furnace (RTA; PEO 601 ATV Technologie GmbH) in an O2 gas flow for 5 minutes.

For the optical energy gap determination UV-vis (Hitachi-U 2000 spectrophotometer; wavelength range 190–1100 nm) spectra were collected. Film thickness and crystal structure of the films were determined from X-ray reflectivity (XRR)
and grazing-incidence X-ray diffraction (GIXRD) data, respectively, collected using the PANanalytical model X’pert Pro diffractometer (CuKα radiation). The crystallite size was calculated from the GIXRD data using full width at half-maximum (FWHM) of the 002 peak and Debye Scherrer’s formula,

\[ D = \frac{0.92}{\beta \cos \theta} \]

where \( D \) is the crystallite size, \( \lambda \) is the X-ray wavelength used, \( \beta \) is the FWHM in radians and \( \theta \) is the Bragg’s angle. Additionally, the dislocation density (\( \delta \)) was evaluated by the formula [51]

\[ \delta = \frac{1}{D^2} \]  

(4)

The surface topography and root-mean-square (RMS) roughness measurements were performed using an atomic force microscope (AFM; TopoMetrix Explorer). The dc resistivity was measured for the films in a linear four-probe configuration. Seebeck coefficient was measured using our home-made setup similar to the one reported in Ref. [52].

**Results**

We first searched for the optimized ALD parameters for the Cu(thd)_2-O_3 process to be able to deposit a series of high-quality thin films with a precisely controlled film thickness. In Fig. 1, we demonstrate for our CuO films the highly linear growth (i.e., film thickness versus number of ALD cycles) behavior expected for an ideal ALD process. To evaluate whether a so-called ALD window exists for our Cu(thd)_2-O_3 process, we plot in the top inset of Fig. 1 the growth-per-cycle (GPC) values for the films at various deposition temperatures from 200 to 260 °C. The GPC value remains almost constant for 200–250 °C. At 260 °C the growth rate decreases rapidly and beyond 270 °C (not shown in the figure) the film growth becomes of the CVD (chemical vapor deposition) type, probably due to partial decomposition of the copper precursor. Based on these results we fixed the deposition temperature to 240 °C for the rest of the experiments. Next we confirmed the self-limiting growth behavior in respect to precursor pulse lengths (and subsequent purge) for both Cu(thd)_2 and O_3 by varying one at a time and keeping the other pulse length fixed to 2 s (and purge length at 3 s). As shown in the bottom inset of Fig. 1 the GPC value remains essentially constant through the Cu(thd)_2 pulse length range investigated. It should be noted however that even though the growth rate remained constant the quality of the films somewhat degraded for the longer Cu(thd)_2 pulses. For ozone, the pulse lengths of 1–2 s yielded the same GPC value but the longer ozone pulses resulted in a rapid increase in the growth rate and simultaneously increased film density, presumably due to decomposition of the precursors. Thus, we fixed the precursor pulse/purge lengths to 2 s and 3 s, respectively.

In Fig. 2, GIXRD patterns are displayed for several as-deposited and annealed films in the thickness range of 9–81 nm. The crystallites size and dislocation density for the annealed films are noted in the respective patterns. The as-deposited films are weakly crystalline and show occasionally traces of Cu_2O as an impurity phase. However after annealing the films in an O_2 gas flow at 400 °C all the CuO gets converted to CuO, as was also reported in literature for Cu-O films deposited by a solution dipping technique [53,54]. As expected the crystallinity enhances not only upon the post-deposition annealing but also with increasing film thickness due to increased crystallites size.

The surface topography and RMS roughness features measured by AFM for the annealed films are shown in Fig. 2(b). In line with the GIXRD data both the surface topography and roughness of the films change due to the structural changes driven by the film thickness and post-deposition annealing effects. The thinnest as-deposited film of 9 nm thickness shows the RMS roughness value of 0.92 nm; then with increasing film thickness the RMS value initially remains essentially the same which may be related to the formation of nano-growth regions before the regular growth starts. Further, as shown in the bottom of Fig. 2(b), the RMS roughness for the thickest film is 1.31 nm.

**Figure 1.** The main figure shows the film thickness versus number of ALD cycles for our CuO films deposited at 240 °C. The top inset shows the growth-per-cycle (GPC) values at different deposition temperatures for 500 cycles. The lower inset shows the GPC values for different pulse (purge) lengths of Cu(thd)_2 and O_3 on left and right y-axes respectively, varying one pulse (purge) pair at a time and keeping the other fixed at 2 (3) seconds.
The high resistivity of the thinnest of these films may be because of two reasons: the low crystallinity and also due to the formation of islands on the surface. The island formation may lead to poor in-plane contacts and thereby increased resistivity for the thinnest film. As the islands grow with increasing film thickness the improved in-plane contacts result in a decrease in resistivity. The island growth also results in crystallites that become larger as the films grow thicker. Since the size of the crystallites is still small (from XRD data) the electrical conduction is mostly dominated by crystallite boundary conduction. Thus the poor crystallinity and resultant poor inter-crystallite connectivity lead to the increase in resistivity of the thicker as-deposited films as is observed in Fig. 3.

Figure 2. (a) GIXRD patterns for as-deposited (lower curves) CuO films and films annealed (upper curves) in O2 at 400 °C. The blue and green lines show the diffraction peaks matched with JCPDS reference data for CuO (JCPDS 00-045-0937) and Cu2O (JCPDS 00-034-1354), respectively. (b) AFM images for as-deposited CuO films.

In Fig. 3 we show the electrical transport data as a function of film thickness for (a) as-deposited and (b) annealed films, and (c) the temperature dependence of Seebeck coefficient and resistivity for the thickest film. The resistivity and Seebeck coefficient of the as-deposited films follow very similar behaviors, first decreasing with increasing thickness and then increasing for the thicker films. The increase in resistivity for the lowest thickness film shows a very similar trend as reported for CuO [45] and Co3O4 [55] films deposited by other techniques. However the value of resistivity for our CuO film is one order of magnitude less than those reported in previous studies [45].

Almost an order of magnitude decrease in the absolute resistivity of the films is observed after the annealing, presumably due to the improved crystallinity. The resistivity remains almost constant at 0.01 Ω·m independent of the film thickness. In Fig. 3(c) we show the resistivity and Seebeck coefficient data as a function of temperature for the thickest film. The temperature dependence of resistivity shows a purely semiconducting behavior with $d\rho/dT < 0$.

Figure 3. Room-temperature Seebeck coefficient and resistivity data for (a) as-deposited and (b) annealed CuO thin films as a function of film thickness. (c) Temperature dependence of Seebeck coefficient and resistivity for the 81-nm thick CuO (annealed) film.
The Seebeck values are positive confirming the p-type conduction of the films.

We present the UV-vis spectra for the annealed CuO films in Fig. 4. For the calculation of the absorption coefficient ($\alpha$) and optical energy gap ($E_g$) from the transmittance (T) and reflectance (R) data shown in the inset of Figure 4(a), we use the same procedure as was reported by us in Ref. [56]. The highest transmittance of ~85% is observed for the thinnest film in the wavelength range greater than 800 nm. The absorption coefficient $\alpha$ decreases with increasing thickness of the films and shows a sharp increase when the wavelength decreases below 800 nm, probably related to the optical gap of the films. As one can find from Fig. 4(b) the indirect optical energy gap increases with the film thickness from 1.06 eV for the thinnest film to 1.24 eV for the thickest film; these energy gap values agree well with the values reported in literature for CuO from both theoretical [57,58,59] and experimental [31-34] studies.

The observed decrease in the optical energy gap with decreasing thickness of the films is in remarkable contrast to the size dependent $E_g$ reported for ZnSe, CdS, ZnO, etc., [6,7,10] where $E_g$ increases with decreasing thickness/radii of the films/crystallites. Since the $E_g$ enhancement has been explained in terms of the increase in the kinetic energy of excitons confined in a nano-size particle, the $E_g$ reduction observed for our CuO thin films suggests that a noble mechanism and/or additional effects should be taken into account. We will discuss this in the next section.

In Fig. 5 we show three plots to perceive the dependence of the optical energy gap on the thickness of the films as usually plotted in literature. The upper inset shows the plot between the optical energy gap and the radii of the crystallites. An unusual linear relation is observed for the cubic root of the radii of the crystallites. The bottom inset presents a linear relation between the thickness and the radii of the crystallites. Thus in the main figure a linear relationship is observed between the optical energy gap and the cubic root of the thickness of the films.

![Figure 4](image1.png)

**Figure 4.** (a) Absorption coefficient as a function of wavelength; the inset shows the transmittance and reflectance spectra for annealed (crystalline) CuO films. (b) Indirect optical energy gap of the films that decreases proportionally with the film thickness. Top inset shows the inverse cubic root dependence of the optical energy gap on the thickness of the films.

![Figure 5](image2.png)

**Figure 5.** The main figure shows the optical energy gap of CuO thin films as a function of cubic root of the thickness (t) of the films. The upper inset shows the optical energy gap as a function of cubic root of the crystallites radius (R) whereas the bottom inset shows the linear dependence between thickness and crystallites radius of the films.

**Discussion**

First, we would like to mention that the Brus model or the modified Brus models [16,17] have unintentionally been proposed for band insulators and may not be suitable for CuO which belongs to the family of Mott-Hubbard insulator systems where onsite Coulomb repulsion plays the dominant role. The molecular cluster method has been applied to describe excitonic states in Mott-Hubbard insulators [60,61]. However, the validity of this method and the quantum
In Brus model charge carriers effective masses play pivotal role in determining the overall optical energy gap shift. For our calculations we decided to choose the effective masses of electrons and holes as calculated by Wu et al. [60]. The reason for this is that the nature as well as the optical energy gap as calculated by them matches almost perfectly to our experimental results. Nevertheless, the overall result, i.e., the increase of optical energy gap with the thickness of the films would not be different even if we employed the parameters calculated by others [31,61]. Wu et al. have calculated different effective masses in longitudinal (0.78) and transverse (3.52) direction due to the non-cubic structure of CuO. However for calculations the longitudinal effective mass was considered with the perspective to estimate the maximum localization energy contribution to the overall optical energy gap shift. For Coulomb energy term the dielectric constant at optical frequency was calculated by the Moss relation [62,63] considering the lowest bulk optical energy gap value of 1 eV [31,33,59,60] in a most pessimistic view to estimate the maximum dielectric constant and hence the lowest Coulomb energy term. Moreover, the calculated dielectric constant value 10 - 0.248 is the materials relative dielectric constant at optical frequency by Zheng et al. [64] for polycrystalline CuO samples.

The Brus model or “effective mass approximation model” was the first model to include the Coulomb attraction between electrons and holes within the crystallites along with the quantum localization energy. Brus [3,10,11] considered the charge carriers (electrons and holes) confined within a potential well equal to the crystallite diameter with an infinite potential barrier outside the crystallite surface. In other words, charge carriers were not allowed to leak through the crystallite surface. According to his model the optical energy gap is

$$E_g(R) = E_g^{bulk} + \frac{\hbar^2}{2R^2} \left[ \frac{1}{m_e} + \frac{1}{m_h} \right] - \frac{1.8e^2}{4\pi\varepsilon_0\varepsilon_r R} - 0.248 \times$$

(5)

where $m_e$ and $m_h$ are the effective electron and hole masses (often being a fraction of the electron mass), $E_g^{bulk}$ is the optical energy gap of the corresponding bulk material, $R$ is the crystallite radius, $\varepsilon_0$ is the permittivity of free space, and $\varepsilon_r$ is the materials relative dielectric constant at optical frequencies. The second term in the equation is the quantum energy of localization (or kinetic energy) that increases as $R^{-2}$ for both electrons and holes, shifting $E_g(R)$ to the higher energies. The third term is due to the screened Coulomb attraction between the electrons and holes; it shifts $E_g(R)$ to the lower energies. The fourth term is size independent and depends on spatial correlation effects; usually this term becomes very small compared to the other two terms and may be neglected.

In Fig. 6 (solid circles) we present the optical energy gap calculated from the Brus model given by equation (5) in the presence of Coulomb attraction as a function of the crystallites radii. The Coulomb attraction term was estimated using the bulk relative dielectric constant ($\varepsilon_r$) equaling to 10. To compare the experimental results with calculations we assumed 1.35 eV [31-34] as the bulk optical energy gap. The lower data points (solid squares) in Fig. 6 show the modified Brus model when the relative dielectric constant was allowed to vary with crystallites radii to fit the experimental data (hollow stars). It should be noted that the dielectric constant was the only one fitting parameter. In order to fit the experimental result perfectly, we allowed the dielectric constant to vary freely. Yet, we obtained a rather small variation of the dielectric constant of 2.6 - 3.0 in the inset of Fig. 6.

In Brus model charge carriers effective masses play pivotal role in determining the overall optical energy gap shift. For our calculations we decided to choose the effective masses of electrons and holes as calculated by Wu et al. [60]. The reason for this is that the nature as well as the optical energy gap as calculated by them matches almost perfectly to our experimental results. Nevertheless, the overall result, i.e., the increase of optical energy gap with the thickness of the films would not be different even if we employed the parameters calculated by others [31,61]. Wu et al. have calculated different effective masses in longitudinal (0.78) and transverse (3.52) direction due to the non-cubic structure of CuO. However for calculations the longitudinal effective mass was considered with the perspective to estimate the maximum localization energy contribution to the overall optical energy gap shift. For Coulomb energy term the dielectric constant at optical frequency was calculated by the Moss relation [62,63] considering the lowest bulk optical energy gap value of 1 eV [31,33,59,60] in a most pessimistic view to estimate the maximum dielectric constant and hence the lowest Coulomb energy term. Moreover, the calculated dielectric constant value 10 - 0.248 is the materials relative dielectric constant at optical frequency by Zheng et al. [64] for polycrystalline CuO samples.
It has been mentioned by Brus [10] that in small optical gap materials, Coulombic attraction gets shielded due to extremely low effective masses of the charge carriers which allow the quantum localization effects to be dominant. However, in CuO the effective masses of both the electrons and the holes are relatively high, which probably results as the dominant Coulomb energy over the quantum localization energy. As usually observed, the optical energy gap increases with decreasing crystallite size (not shown) due to strong quantum localization effects in CuO when the radii of the crystallites decreases below ~4 nm if bulk relative dielectric constant value $\varepsilon_r = 10$ is considered for Coulomb energy calculations. This is roughly in agreement with the calculated Bohr excitonic radius $r_B \approx 1 - 6.6$ nm [60,61] below which the quantum size effects are expected to be dominant as shown by the solid circles in Fig. 6. Moreover, as is evident in Fig. 6, the experimental optical energy gap values denoted by the stars are smaller than the calculated ones. Thus to fit the experimentally observed optical energy gap values with the calculated one we allowed the relative dielectric constant to vary with the radii of the crystallites.

We used this assumption keeping in mind the strong indications in the excitation literature that the dielectric screening should get significantly reduced for small-sized semiconductor nanocrystals [13,18]. The thus obtained dielectric constant is plotted in the inset of Fig. 6, which excellently fit the observed $E_g$, as shown by the solid squares in Fig. 6.

It is said that, in small crystallites the lattice polarization does not follow the more rapid electron and hole motions which results in the reduced dielectric screening of materials. Moreover, Pejova et al. [18] have employed the reduced dielectric screening method in a similar calculation for ZnSe quantum dots. Thus the decrease in the relative dielectric constant value for the calculations is justified. The reduced value of $\varepsilon_r \approx 3$ is consistent with the reported value in ZnSe [18]. Furthermore, this can also be understood from the several literature data; where strong quantum localization effects are reported, even the larger values comparable to bulk relative dielectric constants result reasonably good fit with experiments. In CuO both the quantum localization and Coulomb energy terms are comparable that may also be the reason behind the unusual cubic root dependence between optical energy gap and thickness of the films, as shown in Fig. 5.

To summarize, we would like to say there are still some points to be understood. For example, the role of high dislocation density that causes the dilation in the spacing of atoms may also affect the optical energy gap of materials. In the present case it may not be crucial as the dislocation density is decreasing with increasing film thickness (Fig. 2(a)) which is against the expectation of increase in the optical energy gap of the films with increasing thickness. Furthermore, the role of the defect states that has also been reported to give proportional dependence [39,40]. Gizhevskii et al. [40] have reported the red shift in the optical absorption spectra of nanocrystalline CuO samples due to the presence oxygen vacancies. According to them, these vacancies lead to formation of electron centers via addition of one electron to the main cluster [CuO$_6$]$^-$ which itself acts as a hole center, and the comparable concentrations of the main centers and electron centers cause the red shift of the absorption edge spectra. Moreover, in literature most of the optical energy gap and thickness dependency data are for materials with a direct optical gap. For the indirect-optical gap materials that require lattice phonons to make any band transition the role of lattice phonons are not clear. Thus further experimental and theoretical efforts are needed to fully understand this unusual dependence.

Conclusions

We deposited a series of high-quality CuO thin films in the low thickness range of 9–81 nm, utilizing the inherently excellent capability of the atomic layer deposition technique to produce thin films with a precisely controlled film thickness. An ALD temperature window was found about 220–250 °C for the Cu(thd)$_2$O$_3$ process employed where the growth rate remained essentially constant at ca. 0.17 Å/cycle. The as-deposited films exhibited smooth homogeneous surfaces but were only weakly crystalline. Upon annealing...
the films at 400 °C in O₂ the degree of crystallinity was enhanced.

Electrical transport measurements confirmed the p-type semiconducting behavior of the films. From optical measurements appreciably high transmittance values up to >85 % in the visible range and an indirect optical energy gap of 1.06–1.24 eV were revealed. Most interestingly, an increase in the optical energy gap was observed with increasing thickness of the films.

The data were analyzed using Brus model in the presence of Coulomb attractions between the electrons and holes. The experimental data were in line with the theoretical predictions of the Brus model when the bulk relative dielectric constant was allowed to vary with the size of the crystallites for the Coulomb energy calculations. The plot between the optical energy gap and the film thickness revealed a linear dependence with the cubic root of the thickness (tᵋ/₃) of the films. This type of dependence between the optical energy gap and the film thickness is not very common but in the light of the above discussion it is justified. Furthermore, the results reported here may be true for some other members of highly correlated electron systems, e.g., nanoparticles of γ-Fe₂O₃ for which a red shift to optical energy gap has been explained due to the compression of nanoparticles as a result of surface tension, accompanied by a decrease in the unit cell volume. [65]

The authors thank Prof. Antti Karttunen for his suggestions and discussion regarding the calculation of energy parameters. The present work has received funding from the European Research Council under the European Union's Seventh Framework Programme (FP/2007-2013)/ERC Advanced Grant Agreement (No. 339478) and also from the Aalto Energy Efficiency Research Programme.