

Quantum confinement effect of in-situ generated Cu₂O in a nanostructured zirconia matrix

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The incorporation of Cu²⁺ in zirconyl chloride octahydrate sol or solution was used as a precursor for dip coating. This resulted in the in-situ formation of nanostructured Cu₂O quantum particles in the zirconia matrix. The size-dependent properties of the Cu₂O quantum particles were observed when the films were annealed in the range of 200–600 °C. A red shift of the UV band, ascribed to the transition from the copper d-shells to higher sublevels of the conduction band, was observed in the range of 260–315 nm due to an increase in the nanocrystallite size with increasing annealing temperature. Three types of emissions, blue, green, and yellow, were observed in films of relatively high thickness (around 120–130 nm) due to Wannier-like excitonic transitions. For films of relatively low thickness (50–70 nm) only green emission was observed. From lifetime measurements of samples annealed at 450 °C it may be concluded that the short decay time is bi-exponential in character from ns to ps with the chi-square value of 1.005, which is due to the confinement of Cu₂O quantum particles.

Key words: *sol-gel; nanostructured Cu₂O; quantum confinement; exciton; short-life emission*

1. Introduction

Nano-sized zirconia films can be prepared on silica glass substrates by the sol-gel technique [1]. When the size of the zirconia particles (grains) is in the nano-range (below 250 Å), the meta-stable cubic or tetragonal state of zirconia becomes more stabilized [1]. As a result, the surface area and surface energy increases, facilitating in-situ generation of Zr³⁺ along with oxygen deficiencies in the zirconia system [2, 3]. The generation of trivalent zirconium is possibly due to the formation of oxygen deficient centres in the film in accordance to the following sequence of reactions:



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Incorporation of transition metal ions into the precursor leads also to the formation of a reduced state of the metal ion [4, 5] due to the partial reduction of the metal ion by electrons trapped in oxygen deficient centres.

In the case of the Cu^{2+} system, incorporation leads to the generation of Cu_2O clusters in the zirconia film, Cu_2O exhibiting excitonic behaviour. Excitation-dependent emission spectra of Cu_2O clusters of a particular size have been examined but their size-dependence on excitation wavelengths has not been reported so far. Lifetime measurements of the fluorescence spectra of nano clusters, usually exhibiting a short lifetime, imply excitonic behaviour. In view of the above facts, an attempt was made to synthesize and characterize the size-dependent emission spectra and fluorescence lifetime of Cu_2O microcrystallites in nano zirconia, where both host and dopants are nanosized.

2. Experimental

2.1. Preparation of precursor solution

The precursor solution for films of zirconium oxide-copper oxide was prepared maintaining the atomic ratio, Zr:Cu at 1:1. The starting materials were: recrystallised zirconyl chloride octahydrate (ZOO) and copper(II) nitrate trihydrate in an acidic solvent mixture containing glacial acetic acid (a complexing or polymeric agent). The solvent mixture contained dehydrated ethanol and 2-butanol. The wt. % equivalent of ZrO_2 in the solution was 2.0. The solution was prepared by mixing the requisite amounts of ZOO and Cu(II) salt in the required amount of the acidic solvent mixture while stirring for 2 h. The final solution was green in colour. The sol was aged for five days.

2.2. Preparation of films

The resulting solution was used for the deposition of layers on cleaned Heraeus (Germany) make suprasil grade pure silica glass, adopting a dipping technique with two different withdrawal speeds, namely (i) 4 cm/min (ii) 18 cm/min, to attain films of two different thicknesses. After dipping, the solution layer was formed on both sides of the glass substrate. The coated samples were placed in an air oven and heated at 100 °C for 30 min and then put into a furnace and heated at various temperatures (200°, 300°, 450°, and 600°±5°C) for 30 min in an air atmosphere.

2.3. Characterization

UV-visible absorption spectra of films prepared at various temperatures were recorded at room temperature using a Shimadzu UV-VIS-NIR spectrophotometer (photometric accuracy: ±0.002 Abs in the range of 0.0–0.5 Abs, ±0.004 in the range 0.5–1.0, ±0.3% *T* in transmittance). The thicknesses of the films were measured ellip-

sometrically (Gaertner, L116B). Room temperature fluorescence (lamp-corrected for emission excitation) spectra of the samples were recorded with a Perkin-Elmer Fluorimeter. The fluorescence lifetimes of the multilayer films annealed at 450 °C were measured. For this measurement, a coherent CW mode locked Nd:YAG (Antavs 76 s) synchronously pumped cavity dumped hybrid mode locked Rhodamine 6G dye laser light at 600 nm was used. The fundamental 600 nm laser light was frequency doubled to produce then exciting 300 nm light. The emission was detected at a magic angle (54–74) polarization using a Hamamatsu MCP photomultiplier tube (2809 U) in a time correlated single photon counting set-up. The lifetime of the set-up was 50–60 ps. Microstructure and crystal symmetry (electron diffraction, ED) of the films were analysed by a transmission electron microscope (TEM) (JEOL, JEM-200CX). The accelerating voltage and camera length were 160 kV and 55 cm, respectively.

3. Results and Discussion

3.1. Absorption spectra

It was observed that the precursor solution containing zirconium oxychloride octahydrate and Cu(II) nitrate trihydrate yielded in-situ Cu_2O microcrystallites by the partial reduction of Cu^{2+} caused by trapped electrons in the oxygen deficient nano-zirconia film matrix [3]. These Cu_2O microcrystallites exhibited excitonic transitions in the UV (260–315 nm) (Fig. 1a) and visible (Fig. 1b) regions at room temperature. The absorption bands (UV) of Cu_2O excitons shifted towards longer wavelengths with increasing microcrystallite size, due to the increase in annealing temperature. Microcrystallite sizes can be determined [6, 7] from the excitonic transitions in bulk crystal and microcrystallites. We observed absorption peak shifting due to annealing the film at 200°, 300°, 450°, and 600°C. As the nature of absorption was shoulder-like, we took the 2nd derivative of each absorption and confirmed the absorption peak positions. These were 261 nm, 268 nm, 285 nm, and 288 nm for the above respective annealing temperatures. The microcrystallite size of Cu_2O in the nano zirconia films was evaluated from the shift of the absorption band:

$$E_{\text{QD}} = E_{\text{bulk}} + \frac{h^2}{8MR^2} \quad (3)$$

E_{QD} and E_{bulk} are the exciton energies in the quantum well and bulk, respectively. The simplified form of Equation (3) in terms of the peak wavelength λ and R (the average radius of a microcrystallite) is

$$R = 1.7396 \left(\lambda_{\text{QD}}^{-1} \lambda_{\text{bulk}}^{-1} \right)^{-1/2} \quad (4)$$

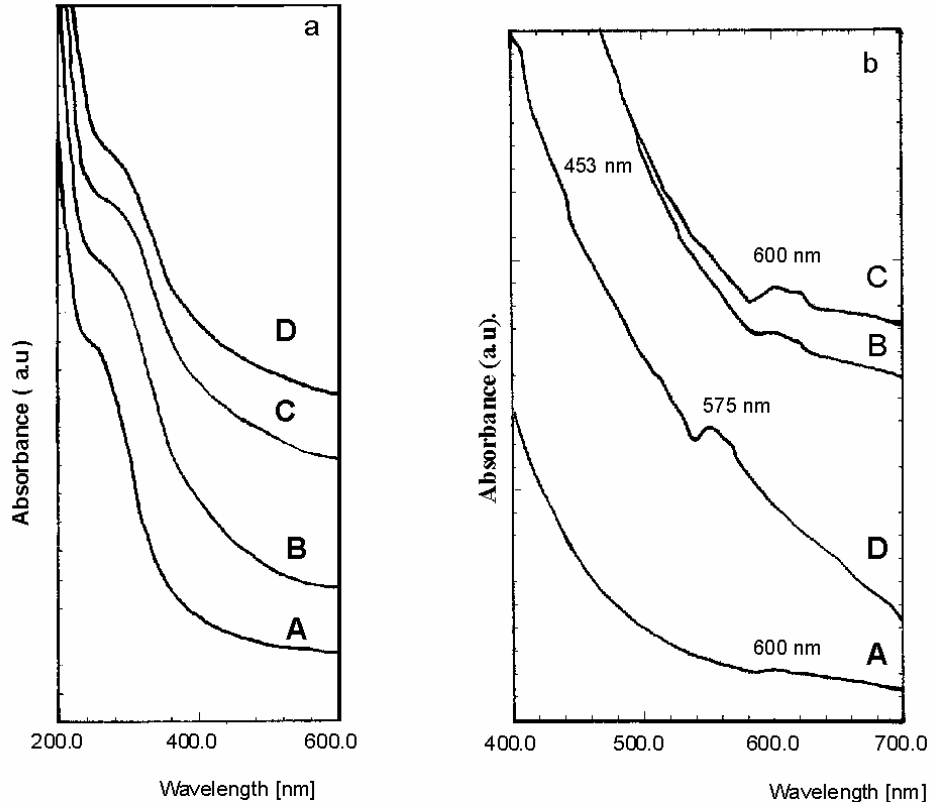


Fig. 1. UV (a) and visible (b) absorption spectra of Cu₂O excitons embedded in a nano zirconia film matrix deposited on a pure silica glass substrate and annealed at: A) 200 °C, B) 300 °C, C) 450 °C, D) 600 °C

We assume the translational reduced mass M of excitons to be $3m_0$, where m_0 is the mass of the electron in vacuum. R and λ are expressed in Å and nm, respectively. The excitonic transition for the bulk was chosen at 371 nm after Jana and Biswas [5]. They observed that the peak at 371 nm does not shift with increasing temperature, i.e., increasing size. The evaluated sizes of the Cu₂O microcrystallites in the corresponding annealing films were 51 Å, 54 Å, 61 Å, 62 Å. We have taken TEM pictures of a typical film annealed at 450 °C (Fig. 2), which indicates that the microcrystallite sizes are in the range of 80–120 Å. The appearance of diffraction rings in the electron diffraction also reveals its crystalline feature, although we did not observe any identifiable 2θ lines in the XRD (not shown here).

The UV bands may be assigned to the transition from the copper d-shells to higher sublevels of the conduction band, as described in the plausible scheme in Fig. 3. In addition to the UV absorption band, a few more absorption bands are observed in the blue, green, and yellow regions. These are expected to be due to Wannier-like excitonic transitions. We did not observe any shifting of these bands due to increasing annealing temperature. They are hydrogen-like, generated from Cu₂O excitons, and

their tentative assignments are shown in the scheme proposed. The absorption band at 600 nm is possibly due to λ_1^Y (first line in the yellow series), but λ_1^G (first line in the

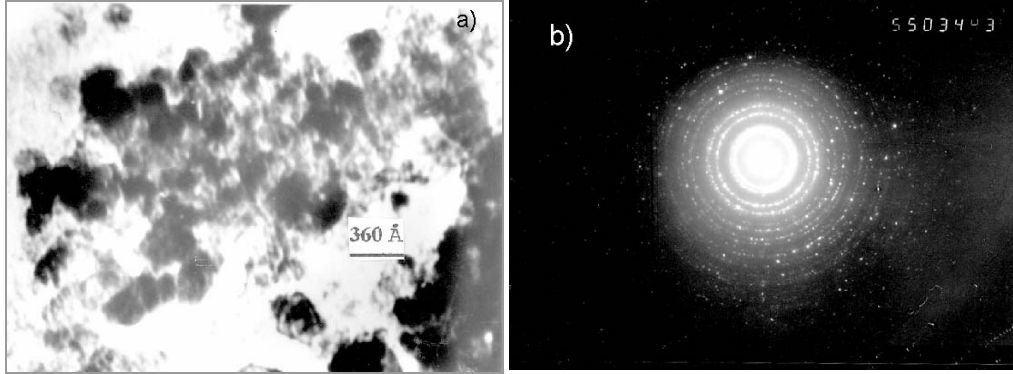


Fig. 2. Transmission electron micrograph (a) and electron diffraction pattern (b) of the film heated at 450 °C

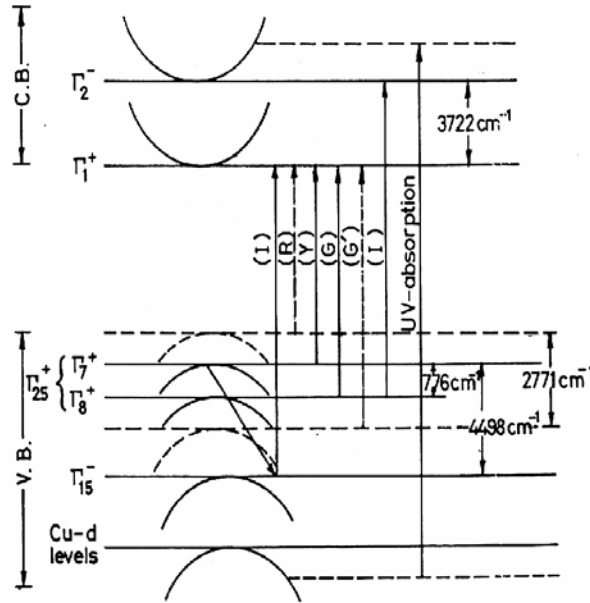


Fig. 3. A plausible path of excitonic transitions in Cu_2O microcrystallites deduced from the absorption bands. The symbols I, Y, and G indicate the indigo, yellow, and green series of excitonic transitions, respectively. G and R represent transitions (dotted lines) from possible sublevels (dotted curves) for green and red, respectively

green series) is not unlikely. Therefore, the band at 555 nm may be assigned to λ_2^G (2nd line in the green series). The transitions of the yellow and green series are partially forbidden direct transitions from Γ_7^+ to Γ_1^+ and Γ_8^+ to Γ_1^+ , respectively, as the valence band

Γ_{25}^+ with the degenerate states Γ_7^+ and Γ_8^+ will split under spin orbit coupling into Γ_7^+ (higher energy state) and Γ_8^+ (lower energy state). Valence band splitting may be obtained from the difference in energy between the yellow ($n = 1$) and green ($n = 1$) series, which is very close to the values reported by other authors [8–13]. In addition, the appearance of a band (Indigo, at 453 nm) in the blue series is possibly due to the transition from Γ_8^+ to an excited conduction band Γ_2^- or to the transition from Γ_{15}^- to Γ_1^+ .

3.2. Luminescence spectra

Excitonic transitions were also evidenced from the fluorescence spectra of the films. We have developed films of two different thicknesses, namely (i) 70 nm and

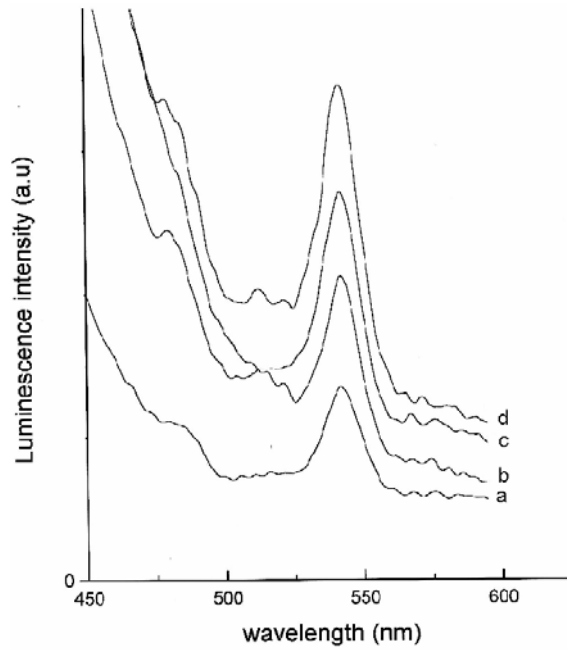


Fig. 4. Emission spectra of films of small thickness, annealed at: a) 200 °C, b) 300 °C, c) 450 °C, d) 600 °C with fixed excitation at 400 nm

(ii) 130 nm. The films of relatively low thickness exhibited a prominent emission peak at ~540 nm (green region) with two shoulders in the blue and yellow regions (Fig. 4). On the other hand, films 130 nm thick exhibited prominent emission peaks in the blue, green, and yellow regions (Fig. 5), which correspond to the emissions of Wannier-like transitions. It is interesting to note that films of the sample annealed at 200 °C, characterized by very small microcrystallite sizes, exhibits only blue and green emissions, although it is relatively thick. The intensity of this green emission decreases with increasing microcrystallite sizes, and the intensity of yellow emission

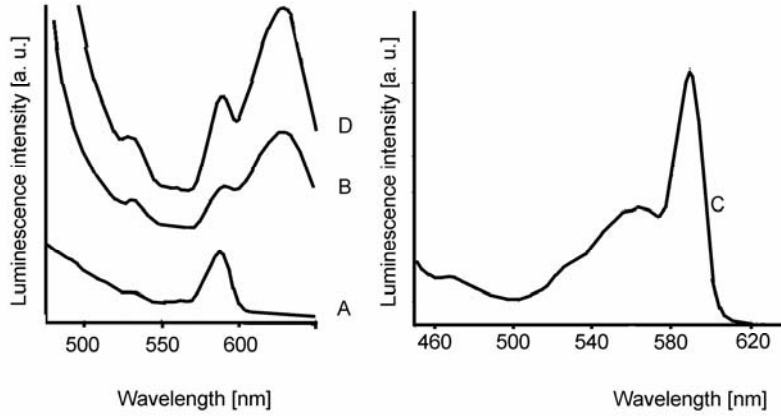


Fig. 5. Emission spectra of films of large thickness, annealed at: A) 200°C, B) 300°C, C) 450°C, D) 600 °C, with fixed excitation at 400 nm

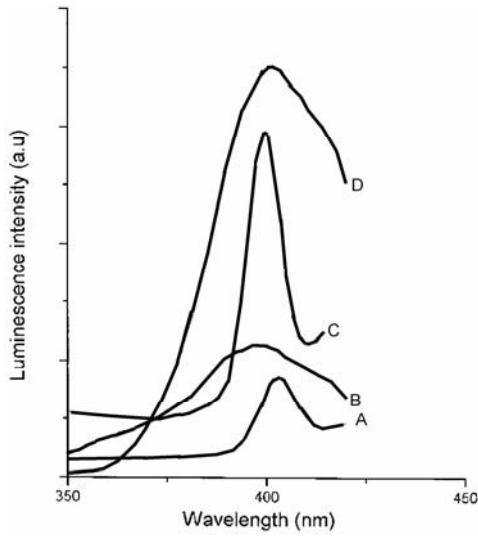


Fig. 6. Excitation spectra of films annealed at: A) 200 °C, B) 300 °C, C) 450 °C, D) 600 °C, with fixed emission at 580 nm

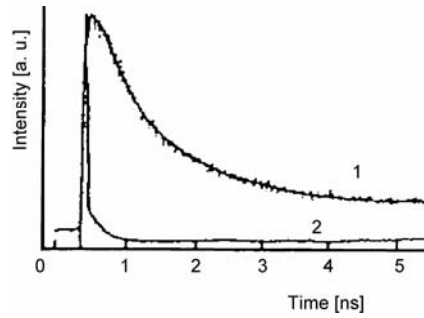


Fig. 7. Experimental fluorescence ($\lambda_{\text{ex}} = 300$ nm) decay curve (1) of a film annealed at 450 °C and the fluorescence decay curve (2) of the lamp used

gradually increases. The above observation was monitored by fixing the excitation wavelength at 400 nm because excitonic transition at 400 nm was observed (Fig. 6) in each case if the excitation wavelength be fixed at the emission peak for yellow region. Although we did not observe any significant excitonic transition in the yellow region of the emission spectra, we observed prominent absorption in that region. It may hence be stated that the yellow emission is possibly due to a 1s excitonic band at ~600 nm. The emissions are expected for the radiation energy from Γ_1^+ to Γ_7^+/Γ_8^+ sublevels, as shown in the Scheme (Fig. 3).

The quantum confinement of Cu₂O microcrystallites was confirmed by the measurement of fluorescence lifetime (Fig. 7) excited with a 300 nm pulsed dye laser. The fluorescence decay was of bi-exponential character with a chi square value of 1.005. The response times were 275 ps and 1318 ps. The short decay corresponded to the existence of quantum confinement [14]. We expect the bi-exponential character is due to the formation of mono-excitons and bi-excitons at the excited state.

4. Conclusion

Cu₂O microcrystallites in nanozirconia film matrix were developed by the sol-gel in-situ method. Films of relatively low and high thicknesses were deposited on pure silica glass to observe the effect of film thickness on excitonic transitions. The quantum confinement effect of the microcrystallites was also observed by the measurement of the fluorescence lifetime.

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