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Cuprous oxide thin films prepared by thermal oxidation of copper layer. Morphological and optical properties

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ABSTRACT

Structural and optical characterization of crystalline Cu_2O thin films obtained by thermal oxidation of Cu films at two different temperatures 800 °C and 900 °C are investigated in this work. X-ray diffraction measurements indicate that synthesized films consist of single Cu_2O phase without any interstitial phase and show a nano-grain structure. Scanning Electron Microscopy observations indicate that the Cu_2O films have a micro-scale roughness whereas High Resolution Transmission Electron Microscopy highlights that the nanocrystalline structure is formed by superposition of nearly spherical nanocrystals smaller than 30 nm. Photoluminescence spectra of these films exhibit at room temperature two well-resolved emission peaks at 1.34 eV due to defects energy levels and at 1.97 eV due to phonon-assisted recombination of the 1s orthoexciton in both film series. Emission characteristics depending on the laser power is deeply investigated to determine the origin of recorded emissions. Time-integrated spectra of the 1s orthoexciton emission reveals the presence of oxygen defects below the conduction band edge under non-resonant two-photon excitation using a wide range of excitations wavelengths. Optical absorption coefficients at room temperature are obtained from an accurate analysis of their transmission and reflection spectra, whereas the optical band gap energy is estimated at about 2.11 eV. Results obtained are of high relevance especially for potential applications in semiconductor devices such as solar cells, optical sources and detectors.

1. Introduction

Cuprous oxide (Cu_2O) is a well-known semiconductor with cubic crystalline structure having a characteristic direct forbidden band gap of about 2.17 eV. The electronic structure of Cu_2O is of considerable interest for a wide range of applications [1,2]. Several interesting properties of this material are related to its rich excitonic structure [1–5] and to the fact that the binding energy of free excitons is relatively large, 150 meV [4]. As a consequence, the exciton radius is small, about 7 Å. Since the excitons are characterized by lifetimes larger than 10 μs in Cu_2O, their coherent propagation through the solid can provide a new type of light source as has been reported by Snoke [5]. This material has attracted increasing interest due to its promising applications in magnetic storage devices [6], photoelectrochemical cells [7], photochemical applications such as catalysts for water splitting [8], gas sensors [9] and biosensors [10]. In addition, Cu_2O sub-microspheres have been reported as advanced electrode material for lithium ion batteries [11]. Furthermore, currently Cu_2O nanocrystals are in focus of many research works because of potential applications in optoelectronic devices operating in the yellow–green region of the spectrum [12]. Numerous characteristics of Cu_2O such as low-cost, cellular inertness, good carrier mobility, relatively high minority carrier diffusion length, high optical absorption coefficient in the visible range and good electrical properties make it attractive in the fabrication of thin film solar cells, with theoretically achievable efficiency up to 20% [13].

Cu_2O is naturally a p-type semiconductor as it contains negatively charged copper vacancies and most likely interstitial oxygen [14]. The p-type conduction property of Cu_2O has been studied for decades and is usually linked to the presence of Cu vacancies (V_{Cu}). In reported experiments the hole states (acceptor-like states) are found in the 0.12–0.70 eV range, above the valence band maximum (VBM) [14–17]. Theoretical studies and ab-initio calculations [18,19] also confirmed that the p-type conductivity is due to the presence of copper vacancies that act as shallow and efficient hole producers and introduce an

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acceptor level at about 0.3 eV above the VBM [18]. Furthermore, a large number of elements were tested as doping impurities. As a result none of n-type conductivity was demonstrated and a most likely explanation for this is based on a self-compensation mechanism [20] or due to the low solubility of the doping impurities [21]. Although the theoretical limit of conversion efficiency in Cu_2O solar cells is relatively high, the maximum obtained by Mittiga et al. in 2006 [22] reached only 2%. This difference might be related to the limited amount of work devoted to this semiconductor and due to the fact that thin film photovoltaic devices composed of p-Cu_2O and n-ZnO received growing attention only in recent years [23,24]. Lately, Minami et al. reported conversion efficiency up to 3.83% in a Cu_2O/ZnO heterojunction solar cell [25]. Due to the lack of clear understanding of the electrical and crystalline properties of this material, combined with observed defects arising in heterojunctions, further optimization of Cu_2O solar cells has been slowed down.

Although Cu_2O has many potential applications in solar energy conversion devices, the major obstacle in technical perspective is the difficult synthesis of thin films with high reproducibility without CuO phase contamination. Therefore, several deposition methods have been used to obtain thin films for further optical characterization, such as thermal evaporation of copper foils [26] or of cuprous oxide powder [27], pulsed laser deposition [28], reactive evaporation [29], or cathodic vacuum arc evaporation [30]. While the fill factor is still limited by the low electric conductivity of the thick Cu_2O substrates, thin films could solve this problem. Among the various elaboration processes, thermal oxidation and sputtering have attracted considerable attention because up to now these two methods lead to new Cu_2O thin structures providing relatively high mobility of the minority carriers. Moreover, the results on reactive sputtering indicated that the formation of phase-pure Cu_2O films is difficult [31].

In this work, Cu_2O thin films were synthesized by thermal oxidation of Cu thin films under controlled conditions. The structural and optical characterizations of these thin films were investigated. X-ray diffraction, SEM and HRTEM microscopy were used to study the influence of the oxidation temperature on the surface morphology and on the nanocrystalline structure of the films. The absorption coefficient was calculated from transmission and reflection spectra. Here, the absorption is due to the superposition of several absorption mechanisms. Photoluminescence measurements were performed at room temperature, using continuous-mode lasers at 325 nm, 473 nm and 532 nm with various output powers. We also investigated the spectroscopic properties of the 1s orthoexciton in Cu_2O films arising from one and two-photon non-resonant excitations under a broad range of experimental conditions.

2. Experimental

2.1. Synthesis of Cu_2O thin films

Cu films were coated on Al_2O_3 (sapphire) substrates by thermal evaporation under vacuum with thicknesses from 1 to 5 μm. Then, the Cu_2O thin films were obtained by continuous thermal oxidation of these Cu films under controlled atmospheric pressure conditions. The thermal oxidation was carried out in a horizontal quartz furnace at 800 °C and 900 °C in a mixture of oxygen and nitrogen during 6 h. The partial oxygen pressure varied from 2 Pa to 20 Pa, chosen to give the Cu_2O phase in accordance with the Cu–O phase diagram [14,17].

2.2. Measurements

Crystalline composition and surface morphology of the deposited samples were studied by X-ray diffraction (XRD) in the θ–2θ mode using Cu-Kα radiation as well as by SEM (JEOL JSM-6320F) and HRTEM (JEOL JEM-3010), respectively. Transmittance and reflectance were measured using a double-beam Jasco V-670 UV-VIS spectrophotometer with an integrating sphere in the 250–1400 nm spectral range. Single photon photoluminescence was carried out using three different continuous-mode lasers with tunable powers: a HeCd laser source at 325 nm with an output power less than 10 mW, a solid state source at 473 nm (LSR473H, Lasever Inc.) with 80 MW maximum output power and a diode-pumped solid state laser at 532 nm with an output power smaller than 1 W (MGLII532). The HeCd laser beam provided a 50 μm spot in the focal plane, with a 0.64 kW/cm^2 power density, without polarization control at 8 mW output power. The 473 and 532 nm laser beams provided 70 μm and 80 μm focus spots, corresponding to 1 kW/cm² and 3.2 kW/cm^2 power densities respectively. The polarization was vertical for the 473 nm source and horizontal for the 532 nm source. Each source was focused on the sample surface using a 100 mm focal length quartz lens. The emitted light was collected by reflection with an angle of 70° regarding the surface normal, collimated and analyzed by a fiber-optic spectrometer (Ocean Optics USB4000-VIS-IR). A tunable mode-locked Ti: sapphire femtosecond laser oscillator (Mai-Tai HP Spectra Physics) at repetition rate of 80 MHz was used for pulsed two-photon excitation in the wavelength range between 690 and 1020 nm. Because multiphoton excitation requires high incident intensities, the laser was focused by a microscope objective (20X/0.40, LD Epiplan Zeiss). The average power of the fundamental laser beam was controlled by a glan polarizer combined with a half-wave plate. In these experiments the fluorescence signal was collected using a short focus, large diameter quartz lens, which was set parallel to the incident laser beam. The luminescence light was transmitted through an appropriate optical filter to eliminate the scattered excitation light and was detected with a gated intensified CCD device (Pi-Max2, Princeton Instruments) coupled to a double grating monochromator (Acton SP500i, Princeton Instruments). All spectra were recorded in the Visible near IR region at room temperature, whereas during all interrelated measurements, the laser power was fixed.

3. Results and discussion

3.1. Surface morphology

Each Cu_2O film presents a rough surface depending on the oxidation temperature. The oxygen partial pressure did not lead to any remarkable change on the surface morphology. High resolution SEM images obtained at 3.0 kV are shown in Fig. 1. The surface of the films presents a microcrystalline structure with grain sizes of about 5–10 μm and 5–15 μm for samples obtained at 800 °C and 900 °C respectively (Fig. 1S). The surface of the films is decorated by numerous holes of about 1 μm size probably formed by morphological defects at the initial grain boundaries of the Cu film (Fig. 2S). From these images we also point out the presence of small elongated crystallites (100–500 nm) on the surface of the films. The general orientation of the grains can be seen in Fig. 1(and Fig. 1S). The white contrast indicates preferential grain growth direction probably induced by thermal gradient during annealing. A mean grain roughness of about 150–400 nm can be estimated from images taken at higher magnification, as shown in Fig. 1. It is interesting to note that the 800 °C annealing resulted in the formation of relatively smooth terraces on the top of the grains and of relatively smooth borders at the intersection of grain boundaries. Occasionally, a nanostructuration can be observed at the edge of microcrystals (Fig. 1a). However, this effect is enhanced if the oxidation process occurs at 900 °C, inducing a strong surface nanostructuration (Fig. 1b).