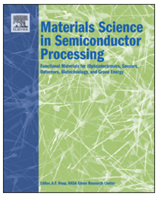
Materials Science in Semiconductor Processing 26 (2014) 527–532

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp



Development of transparent conducting copper and iron co-doped cadmium oxide films: Effect of annealing in hydrogen atmosphere

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ARTICLE INFO

Available online 6 June 2014

PACS:
78.20.Ci
72.20.−i
78.70.En

Keywords:
Cadmium-iron-copper oxide
Fe- and Cu-doped CdO
Co-doping
TCO

ABSTRACT

Hydrogenated (annealed in hydrogen atmosphere) cadmium oxide (CdO) thin films co-doped with iron (Fe) of different levels and fixed (2.5%) copper (Cu) amount were deposited on glass and silicon wafer substrates by thermal evaporation. The films were characterised with X-ray fluorescence, X-ray diffraction, optical spectroscopy, and dc-electrical measurements. The obtained results show important improvements in the conductivity, mobility, and carrier concentration compared to un-doped and non-hydrogenated CdO. Hydrogenated CdO doped with 2.5% Cu and 1.3% Fe improved the conductivity (2293.6 S/cm) by ~46 times, mobility (78.31 cm^2/V s) by ~11 times, and carrier concentration (1.82×10^{20} cm^{-3}) by ~4 times. This suggests the possibility of using CdO:Cu:Fe–H as transparent-conducting-oxide and dilute-magnetic-semiconductor field of applications.

1. Introduction

The conduction and optical properties of transparent conducting oxides (TCO) can be controlled by doping with foreign metallic ions. Furthermore, doping could create in TCOs not native properties, such as magnetic, optical, optoelectronic, etc., that would broaden the frame of TCO applications. Cadmium oxide (CdO) is one of the n-type TCOs with a resistivity of ~10^{-2}–10^{-4} Ω cm and good transparency especially in the near infrared (NIR) spectral region with a direct bandgap of ~2.2–2.7 eV [1–3]. Doped CdO films have many optoelectronic applications as TCO in solar cells, smart windows, and in many other applications [1,2,4,5]. One of the possible applications of doped CdO would be a dilute magnetic semiconductor (DMS), which needs dopants of transition metals (TMs) such as iron (Fe), cobalt, or rare earths [6]. Generally, DMS materials must have ferromagnetic behaviour that could be used in spintronic applications. It was observed [7] that doping CdO with nickel ions creates paramagnetic and ferromagnetic (FM) properties. One of the accepted scenarios for explanation the appearance of DMS is the magnetic interaction between dopant TM ions, which substitute cadmium (Cd) ions, via itinerant electrons (Ambulant electrons carrying magnetic interaction) in CdO. Such carrier mediated magnetic interaction give rise to an effective FM coupling between TM spins.

Doping CdO with metallic ions like copper (Cu^{2+}) of smaller size compared to Cd^{2+} (ionic radius of Cd^{2+} and Cu^{2+} are 9.5×10^{-2} nm and 7.3×10^{-2} nm, respectively [8]) could improve conduction parameters [9], especially the carrier mobility, like the case with germanium- or tungsten-doped CdO [10,11]. Therefore, it is possible to

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http://dx.doi.org/10.1016/j.mssp.2014.05.015
1369-8001/

investigate co-doping of CdO with TM Fe ions and metal Cu ions, i.e. CdO:Cu:Fe thin films. Furthermore, hydrogenation of CdO:Cu:Fe samples further improves the conduction parameters. The present study focuses on structural, electrical and optical investigation of hydrogenated Cu- and Fe- codoped CdO films (CdO:Cu:Fe–H). To the best of our knowledge, this study on the hydrogenated CdO:Cu:Fe films are carried out for the first time.

2. Experimental part

Cu and Fe-codoped CdO thin films were deposited on glass substrates and silicon (Si) wafers in a high vacuum chamber using a successive thermal deposition method of the starting materials. The glass substrates were ultrasonically cleaned whereas Si wafers were chemically cleaned using acid (HF). CdO powder was evaporated from an alumina basket (Midwest Tungsten Service, USA) while Cu- and Fe-acetylacetonate (from Fluka A.G., Germany) powders were sublimated by a heated Pyrex crucible. A certain amount of Cu- and Fe-acetylacetonate mixture was first deposited forming a layer on the substrate, and then a CdO over-layer was deposited. The evaporated masses were controlled during preparation with a piezoelectric sensor, i.e. the preliminary control on the elemental content is done by the evaporated quantity and by using piezoelectric sensor. To decompose the complexes and form CdO:Cu:Fe crystalline films, the as-grown films were annealed at 400 °C for 1 h in air following by natural cooling inside the closed oven to room temperature. For hydrogenation, the as-prepared films were annealed in pure hydrogen at 300 °C for 20 min, thus forming CdO:Cu:Fe–H films.

The film thicknesses as measured after annealing by an MP100-M spectrometer (Mission Peak Optics Inc., USA) was found to be in the range 0.2–0.3 μm. An energy dispersion X-ray fluorescence (EDX) method was used to determine the relative weight fraction of Cu and Fe to Cd in the films. The crystal structure was determined using an X-ray diffraction (XRD) method by using an Ultima IV Rigaku high resolution X-ray diffractometer equipped with Cu-Kα radiation (λ=0.11548 nm). The spectral optical corrected transmittance, $T(\lambda)$, and reflectance, $R(\lambda)$, were recorded at normal incidence in the UV–vis–NIR spectral region (300–3000 nm) using a Shimadzu UV-3600 double beam spectrophotometer. The dc electrical parameters (ρ, μ, and N_{el}) were measured by using a standard the van-der-Pauw method with a magnetic field of ~1 T. As mentioned in [12], when the donor concentration is larger than 10^{19} cm^{-3} then the contact resistance decreases rapidly and could be neglected, which is the case in the present Al/CdO:Cu:Fe contact (We should mention as a remark that when donor concentration is less than 10^{17} cm^{-3}, then the current is mainly due to the thermionic emission and the contact resistance is high and cannot be neglected).

3. Results and discussion

3.1. Chemical composition

Fig. 1 illustrates the energy-dispersive X-ray fluorescence (EDX) spectrum of the prepared Cu-and Fe-doped CdO thin films deposited on Si wafer. The spectrum shows the Cd L-spectrum (3.13–3.53 keV), Cu Kα-signal (8.04 keV), Fe Kα-signal (6.40 keV), and Si Kα substrate signal. The ratio of integral intensity of Cu Kα (I_{Cu}) and Fe Kα (I_{Fe}) to that of Cd L-signal (I_{Cd}) or (I_{Cu}/I_{Cd}) and (I_{Fe}/I_{Cd}) was used to determine the relative mass fraction of Cu and Fe to Cd in each film. For that purpose, the well-known method of microradiographic analysis was used [13]. The reference films were pure Cu, Fe, and CdO thin films. Films with a fixed Cu content of ~2.5% and different Fe mass ratio contents, (Fe/Cd)% ~1.1%, 1.2%, 1.3%, 1.4%, and 1.5%, were investigated (the films were referred by their relative Fe% content).

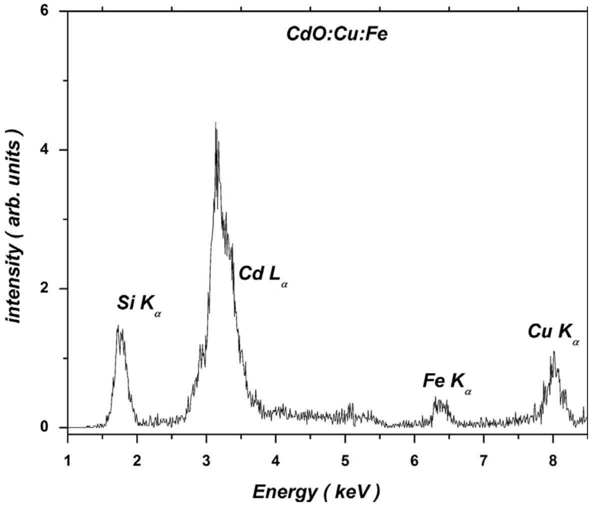

Fig. 1. X-ray fluorescence spectrum for CdO:Cu:Fe–H film.

3.2. Structure analysis

Fig. 2 shows XRD patterns of CdO:Cu:Fe–H films with that of pure CdO for comparison. It can be observed that all the investigated films are polycrystalline of cubic (Fm-3m) CdO structure with lattice constant of around 0.468 nm, which is close to the JCPDS value (0.46948 nm) for pure CdO [14]. All the investigated CdO:Cu:Fe–H films including pure CdO have [111] relative preferred orientation growth. However, it can be noticed that the [111] relative preferred orientation (RPO) depends on Fe content. To evaluate the [111] RPO strength, the following intensity ratio

$$RPO = I_{(111)}/[I_{(111)}+I_{(200)}+I_{(220)}+I_{(311)}] \quad (1)$$

was used. As shown in Fig. 3, Fe doping enhanced the [111] orientation growth, especially with concentration of 1.2–1.3% where the [111] RPO has its highest relative values. The [111] RPO might be also used also to evaluate the films crystallinity.

In order to study the effect of doping on the host CdO unit cell volume ($V_{cell}=a^3$), the film with ~2.5% Cu-doped CdO was prepared by the same method. The inset of Fig. 3 shows that Cu incorporation into CdO crystal lattice reduces V_{cell} of the host CdO, due to the lower ionic radius of Cu^{2+} in comparison to that of Cd^{2+}. Due to the lower ionic radius of Fe^{2+} (0.092 nm [8]) compared to Cd^{2+}, the substitution of