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ساخت لایه نازک اکسید رسانای شفاف نوع p با سختی بالا جهت استفاده به عنوان آندهای محافظ در صفحات نمایش تخت

سید مرتضی احمدی، شهاب شریفی مالواجردی، مرتضی عاصمی و مجید قناعت‌شعار

آزمایشگاه نانومغناطیس و نیمرساناهای مغناطیسی، پژوهشکده لیزر و پلاسما، دانشگاه شهید بهشتی، اوین، تهران

m_amolasaraei@sbu.ac.ir, shsh1292@hotmail.com, asemi.physics@gmail.com, m-ghanaat@sbu.ac.ir

چکیده- در این تحقیق، لایه نازک اکسید رسانای شفاف نوع p با سختی بالا که قابلیت استفاده به عنوان شیشه رسانای محافظ در صفحات نمایش را دارد، ساخته و مشخصه‌یابی می‌شود. به همین منظور، ابتدا ماده هدف دلافوسیت $CuCrO_2$ آلاییده با ۲/۵ درصد منیزیم به روش واکنش حالت جامد ساخته شده و سپس با استفاده از کندوپاش RF از آن لایه نازک بر روی زیر لایه کوارتز تهیه می‌شود. این لایه نازک که می‌تواند نقش اتصال مثبت در ساختار صفحات نمایش را بازی کند، دارای شفافیت در بازه مرئی حدود ۶۷٪، رسانندگی الکتریکی برابر ۱۰/۵ زیمنس بر سانتی‌متر و سختی ۹۵۰ ویکرز است.

کلید واژه- سرامیک شفاف سخت، اکسید رسانای شفاف، دلافوسیت، صفحه نمایش

Fabrication of p-type transparent conducting oxide with high hardness for application as protective anode in flat panel displays

Morteza Ahmadi, Shahab Sharifi Malvajerdi, Morteza Asemi, Majid Ghanaatshoar

Laser and Plasma Research Institute, Shahid Beheshti University, Evin, 1983969411, Tehran, Iran

m_amolasaraei@sbu.ac.ir, shsh1292@hotmail.com, asemi.physics@gmail.com, m-ghanaat@sbu.ac.ir.

Abstract- In this research, a p-type transparent conducting oxide with high hardness is prepared. Samples have been analysed to investigate their optical and electronic properties, crystal structure and the hardness of the layer. The formed layer was revealed to have potential applications as protective conducting glass in electronic displays. For this purpose, 2.5% Mg-doped $CuCrO_2$ delafossite target was prepared using solid-state reaction method. The target was then used to deposit a $CuCrO_2$: Mg thin layer on quartz substrates using RF sputtering. The prepared thin film that can play the role of a positive electrode in displays has a transparency in the visible region of about 67%, an electrical conductivity of 10.5 Scm^{-1} and a mechanical hardness of about 950 Hv.

Keywords: Hard transparent ceramic, Transparent conducting oxide, Delafossite, Display.

1. Introduction

Transparent conducting oxides (TCOs) are an important component of many technologies such as photovoltaics, low-emission windows, electromagnetic shields and flat panel displays [1]. The above mentioned applications are made possible due to the simultaneous conductivity and optical transparency of these materials [2]. Generally, TCOs are grown as thin films that require certain substrate properties. By forming TCO with layers that have a high hardness, the need for protective thick glasses and encapsulation of the inner circuits is effaced [3].

In previous years many methods have been utilized to protect devices from oxidation, wear, and other damages made via atmospheric gas interactions. For this purpose transparent polycrystalline SiO_2, silicon, and glasses with high thickness up to 20 μm have been grown on top of devices [4]. Among transparent conducting oxides, n-type TCOs are more developed and the need for their p-type counterparts is sensed. Delafossite materials have shown the best simultaneous transparency and p-type conductivity [5].

$CuCrO_2$ is a delafossite material containing Cr atoms that is a refractory metal with high hardness even in the form of an oxide. Comprising Cu atoms, which lead to high electric conductivity, $CuCrO_2$ becomes a good candidate as hard TCO layer with the energy band gap of 3.25 eV [6]. In this paper, we are aiming to deposit Mg-doped $CuCrO_2$ to obtain a hard TCO. By doing so, this material will have potential features to take the place of nowadays protective glass and non-conductive thin layers used for encapsulation of some electronic devices.

2. Experiment

In order to prepare $CuCr_{0.975}Mg_{0.025}O_2$ target we employed solid-state reaction method. High-purity oxide powders of copper, chromium and magnesium were mixed in stoichiometric ratio and milled for 10 hours using a ball milling system. The resulting powder was pressed into a 2-inch pellet by a hydraulic press and sintered in an air furnace at 1250 °C for 12 hours. The target was placed in a DST3 RF sputtering system and Mg-doped $CuCrO_2$ thin film was prepared on quartz substrate. The sputtering was performed with 150 W RF power in an argon pressure of 3.3×10^{-3} Torr for 1.5 hour. During deposition, the quartz substrate was heated to ~300 °C for better adsorption and homogeneity. To improve the crystallinity of the films and achieving the delafossite phase, post-deposition annealing was performed in a high vacuum furnace at 800 °C for 2 hours.

The grazing incidence X-ray diffraction (XRD) analysis was carried to identify the crystalline formation of the sample using a Philips PW1730 instrument. An atomic force microscope (AFM) was used to investigate the Nano hardness of the layer by a Nano Scope III from Digital Instruments AFM. Field emission scanning electron microscopy (FESEM, TESCAN mira 3 xmu) was utilized to realize the morphology of the prepared thin film. Furthermore, the UV-vis transmittance spectrum of the prepared thin film was recorded using an Avantes UV-vis spectrometer (AvaSpec-3648).

3. Results and discussion

In order to investigate the crystal structure of the thin film, we employed XRD analysis in grazing configuration which is shown in Fig 1. As we can see from the figure, the amorphous nature of quartz substrate is clear in the background noise but a distinct peak is observed at 2θ=36° which corresponds to the formation of $CuCrO_2$ rhombohedral phase alongside the (012) plane. The crystallite size of thin films, calculated by Debye-Scherrer formula was about 25 nm.

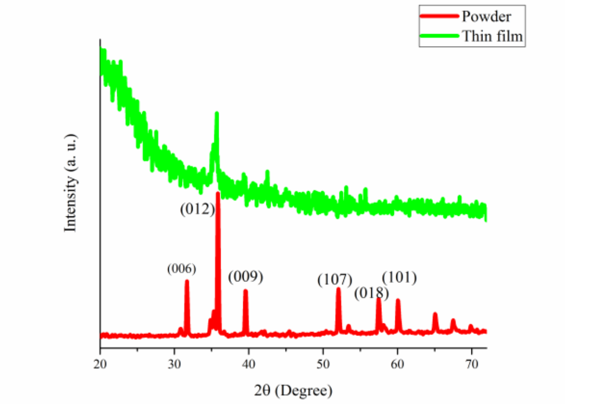

Figure 1: Grazing XRD patterns of Mg-doped $CuCrO_2$ powder and thin film

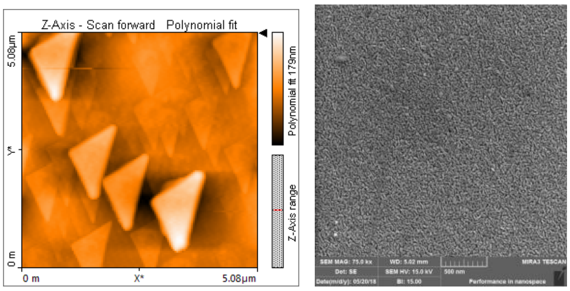

Figure 2:AFM & FESEM micro and nano-graphs of the deposited sample

We used both AFM and FESEM analysis to examine the surface morphology of the thin film. The AFM micrographs illustrated the formation of triangles on the surface of the film which corresponds to the rhombohedral phase of $CuCrO_2$. Whereas the FESEM nano-graphs showed that the surface of the thin film is smooth and homogenous which is necessary for a layer with high transparency and hardness.

The optical properties of the thin film were analyzed by UV-visible spectroscopy and the bandgap of the film was acquired from absorption spectrum by Tauc formula which are shown in Fig. 3. As we can see from the figure, the film has a high transparency of about 70% in the visible region and so is suitable for transparent applications. This high transparency is the result of 3.25 eV bandgap of the material which prevents the visible light photons (2.1 to 3.1 eV) from being absorbed.

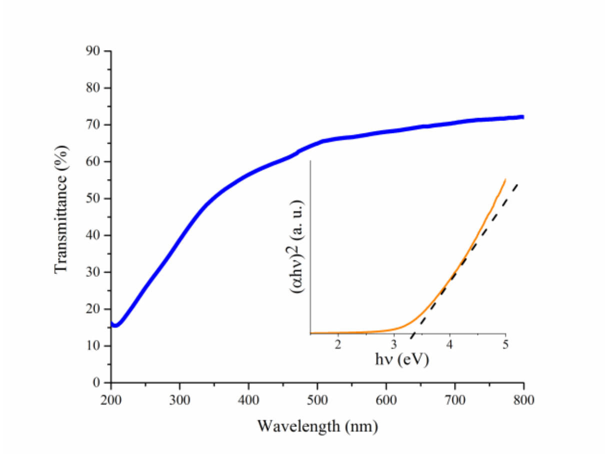

Figure 3: Transmittance spectrum of the prepared thin film and the bandgap acquired from Tauc formula (inset)

In order to investigate the electrical properties of the material, we employed Hall measurement at room temperature in Van-der Pauw configuration. The result of this measurement which is shown in Table 1, indicated the p-type conductivity of the material with the amount of 10.41 Scm^{-1} that is considered a high conductance among p-type TCOs [7].

Table 1: Electrical properties of the thin film

Material	Mobility ($cm^2 V^{-1} s^{-1}$)	Hole concentration (cm^{-3})	Conductivity ($S cm^{-1}$)
$CuCr_{0.975}Mg_{0.025}O_2$	0.018	3.06×10^{20}	10.41

The hardness of the deposited $CuCrO_2$ thin film was investigated by nano indent AFM hardness measurement (Fig. 4). The gained hardness was 9.5 GPa which is approximately 950 Hv. This hard layer is in great comparison with previous attempts made for the formation of hard $CuCrO_2$ which had hardness up to 750 Hv [8]. Amorphous Al_2O_3 coatings have had hardness up to 900 Hv but have only been able to be applied as a hard protective layer solely [9] while the $CuCrO_2$ layers prepared in this research show potential electronic, optical and mechanical properties for the use in touchscreen displays.

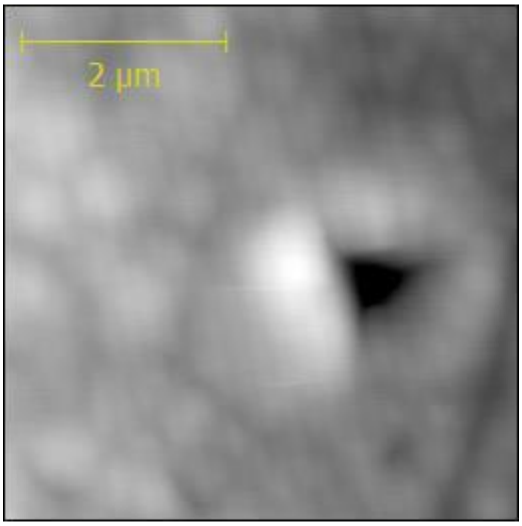

Figure 4: Nano indent AFM hardness measurement image

4. Conclusion

In this paper, we prepared a p-type TCO with high figure of merit properties. This material showed a high transparency of ~70%, electrical conductivity of ~10.5 Scm^{-1} and a hardness of 950 Hv. These properties together make this TCO very suitable for application in flat and touch displays that can protect the inside circuitry from damages, and conduct electricity while being invisible to the eye.

Acknowledgement

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