Materials Letters 216 (2018) 88–91

Contents lists available at ScienceDirect

Materials Letters

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

Hydrated magnesium-carbon films with conductivity and wide-range visible-to-far-infrared transparency

Shuai Guo [a,1], Lei Yang [c,1], Bing Dai [a], Fangjuan Geng [a], Zhenhuai Yang [a], Pei Lei [d], Peng Wang [a], Gang Gao [a], Jiecai Han [a], Victor Ralchenko [a], Jiaqi Zhu [a,b,*]

[a] Center for Composite Materials and Structures, Harbin Institute of Technology, Harbin 150001, China
[b] Key Laboratory of Micro-systems and Micro-structures Manufacturing, Ministry of Education, China
[c] Center of Analysis Measurement, Harbin Institute of Technology, Harbin 150001, China
[d] Beijing Institute of Aeronautical Materials, Beijing, China

ARTICLE INFO

Article history:
Received 2 November 2017
Received in revised form 21 December 2017
Accepted 23 December 2017
Available online 24 December 2017

Keywords:
Infrared transparent conductive films
Hydrated magnesium-carbon films
Mg_x-C_y films
Sputtering
Electrical properties

ABSTRACT

The hydrated magnesium-carbon films fabricated in this study are the novel-innovative non-oxide-type transparent electronic material. The films, which have a structure similar to that of magnesium hydroxide, were produced by making Mg_x-C_y films deposited by magnetron co-sputtering react with water vapor. As the extrinsic defect of hydration magnesium-carbon films, C atoms provided redundant electrons, resulting in a conductivity of approximately 3.31×10^{-2} Ω·cm. Although the conductivity of hydrated magnesium-carbon films is not prominent comparing to the conventional and widely-used n-type TCO materials, e.g. ITO, the films also showed excellent optical properties, which can be attributed to their low bond energy, with the infrared transmittance of the films being greater than 72% for a plasma wavelength of approximately 10 μm. By varying the atomic C content of the films, a visible-region transmittance greater than 80% could be realized. The optical bandgap of the films was approximately 4.04–6.87 eV and was blue-shifted because of the Moss-Burstein effect.

1. Introduction

Transparent and conductive films (TCFs) that are transparent in the visible range and simultaneously exhibit desirable electrical properties are in high demand for use in touch screens, solar cells, plasma displays, organic light-emitting diodes, and information storage devices [1–3]. These films are usually of a wide-bandgap oxide, such as ZnO, In_2O_3, SnO_2, or CdO [4–9]. However, the poor infrared transmittance of these films limits their applicability in the infrared range. According to Drude's free-electron theory, these films need to have a low carrier concentration, if they are to exhibit desirable transmittance in the infrared range and, in particular, in the mid-infrared and far-infrared regions. However, a low carrier concentration results in poor conductivity, making the films unsuitable for use in some semiconductor devices. Thus, one has to strike a balance between the infrared-region transparency and conductivity of the films.

It is known that magnesium hydroxide shows excellent visible and infrared-range optical properties because of its special valence band and structure [10]. However, magnesium hydroxide is an insulator. On the other hand, the conductivity of magnesium-carbon alloys is better than that of TCOs. However, magnesium-carbon alloys are opaque in the infrared region. Thus, in this study, we used a two-step method to prepare infrared-transparent and conductive hydrated magnesium-carbon films. During the synthesis process, we could control the carrier concentration and mobility by adjusting the temperature and water vapor content as well as the reaction time. The obtained results confirmed that the method allows for the realization of films with improved photoelectric properties.

2. Experimental procedures

In the first step, Mg_x-C_y films were deposited on quartz, and zinc sulfide substrates by magnetron co-sputtering. Then, in the second step, the films were then made to react with water vapor. This yielded hydrated magnesium-carbon films. Separate magnesium and carbon targets were used as the Mg and C sources, respectively. The vacuum chamber was evacuated to a base

* Corresponding author at: Center for Composite Materials and Structures, Harbin Institute of Technology, 2 Yikuang Road, Harbin 150001, China.
E-mail address: zhujq@hit.edu.cn (J. Zhu).
[1] These authors contributed equally to this work.

https://doi.org/10.1016/j.matlet.2017.12.112
0167-577X/

pressure lower than 10^{-4} Pa by combination of a turbo-molecular and a rotary pump. During the film deposition, the argon pressure was fixed at 0.5 Pa by the combination of a throttle valve and an argon flow controller. Mg_x-C_y films with different C contents were prepared by changing the deposition power used radio frequency as the extrinsic atoms. Mg was deposited using a direct current power of 4.8 W. As stated above, the hydrated magnesium-carbon films were obtained by making the Mg_x-C_y films react with water vapor.

The surface morphology was measured by atomic force microscope (AFM, Bruker dimension icon) in contact mode at atmospheric temperature and pressure. The surface morphology of these films was examined by scanning electron microscopy (SEM, FEI Helios Nanolab 600i). The crystalline structures of the films were observed using glancing incident X-ray diffraction (GIXRD) analysis (Empyrean, PANalytical), in order to determine their morphologies and crystallinities. Fourier transform infrared spectroscopy (FTIR, PerkinElmer) was used to measure the transmittance spectra of the films formed on zinc sulfide substrates. Ultraviolet–visible spectrophotometry was employed to investigate the visible-region optical properties of the films. Finally, the electrical properties of the films were characterized by Hall measurements, which performed in the Van der Pauw geometry using an Ecopia HMS-3000 Hall measurement system.

3. Results and discussion

Microstructure characterization by SEM (Fig. 1(a)) was conducted to understand the surface morphology of magnesium-carbon films. The films show uniform and well developed grains distributed over the entire surface. Atomic force micrographs of 1 μm thick magnesium-carbon films prepared on glass substrates are shown in Fig. 1(b). The films exhibit a root mean squared roughness (*Rq*) of 4.64 nm over a 1 μm×1μm area that translates to flat surfaces. Fig. 1(c) presents the XRD patterns of the Mg_x-C_y films formed on quartz substrates by magnetron co-sputtering at room temperature using different sputtering powers for the C target. The Mg_x-C_y films have a hexagonal crystal structure (space group: P63/mmc(1 9 4), PDF file No. 35-0821) and exhibit a high-intensity (0 0 2) peak. In addition, the crystallinity of the films decreases with an increase in the sputtering power; this can be ascribed to the fact that the C atoms prevented the growth of Mg crystals. After the completion of the first step, in order to ensure that the Mg_x-C_y films had a structure similar to that of hydroxide, the films were made to react with water vapor at 100 °C in a reaction kettle. The difference in the crystallinities of the hydrated magnesium-carbon films after the second step was confirmed by their XRD patterns, as shown in Fig. 1(d). In picture, the (0 0 1) peak related to the hexagonal structure of $Mg(OH)_2$ (space group:

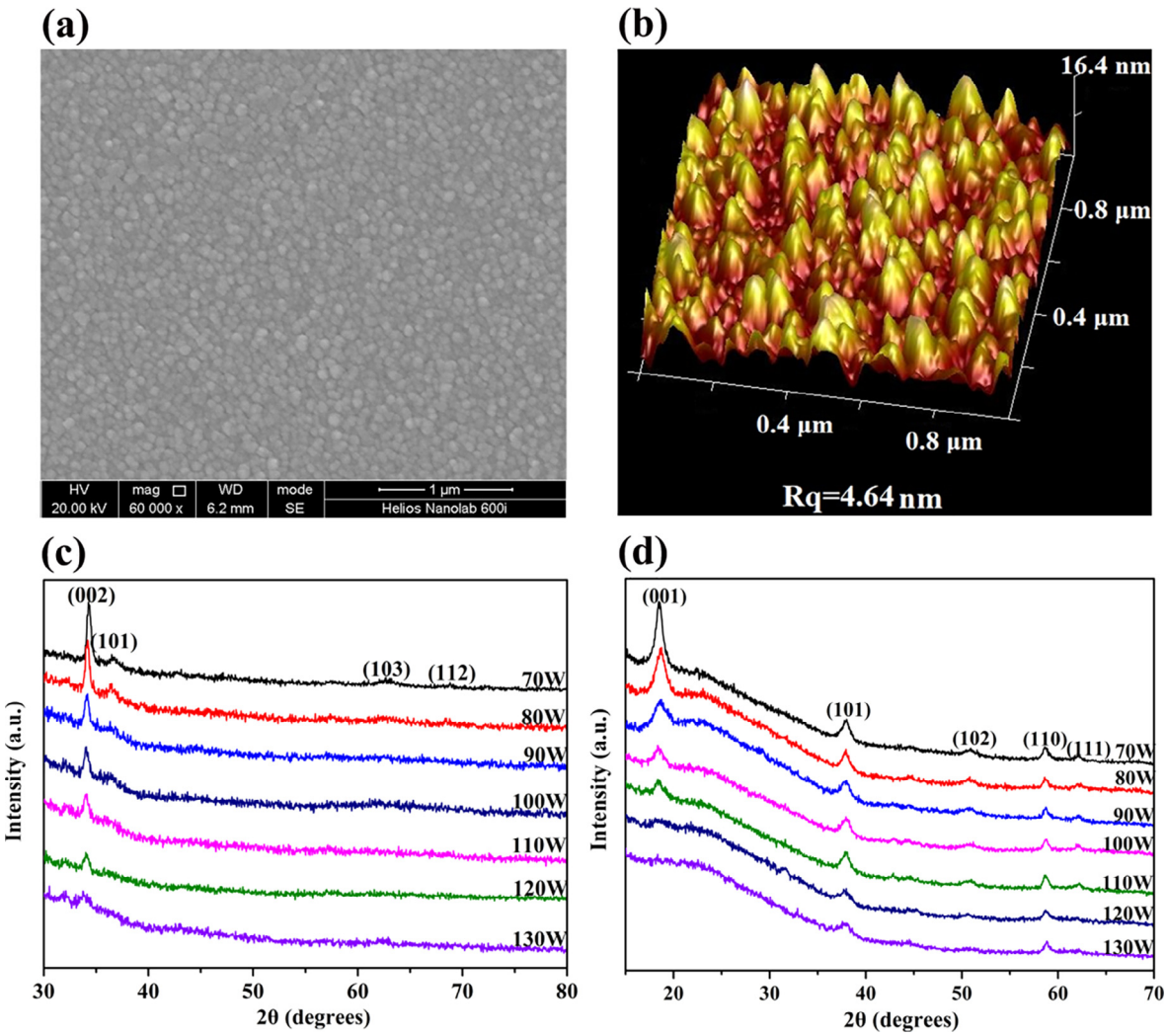

Fig. 1. Surface morphology and crystal structure of magnesium-carbon films: (a) High resolution SEM surface image; (b) Atomic force microscope topography of magnesium-carbon films; (c) GIXRD patterns of Mg_x-C_y films formed at different C target sputtering powers; (d) GIXRD patterns of hydrated magnesium-carbon films formed at different sputtering powers;