Novel Rare-Elements Free Transparent Conductor of $\text{Mg}(\text{OH})_2\text{-C}$ Compounds*

Takamitsu Honjo, Masafumi Chiba, and Toshiro Kuji†

Course of Science and Technology, Graduate School of Science and Technology,
Tokai University, 317 Nishino, Numazu, Shizuoka 410-0395, Japan

(Received 9 November 2008; Accepted 27 May 2009; Published 25 July 2009)

We are now reporting that Mg-C-O-H compound which has a Mg hydroxide symmetry, $\text{Mg}(\text{OH})_2$, whose mineral name is Brucite, is an excellent electrical conductor with high optical transparency. We believe that this new material is the first non-oxide type transparent conductor. The compound has approximately 90% of optical transmission and conductivity of approximately $10^{-2} \Omega\text{cm}$ with $2.4 \mu\text{m}$ of thickness. The compound was fabricated through two consecutive processes. First Mg-C films were prepared by magnetron sputtering. Then, post-treatment was done to make the Mg-C react with moisture in the air. These processes yielded $\text{Mg}(\text{OH})_2\text{-C}$. In this paper, the fabrication processes and optical and electrical conductive properties of the compound will be reported and possible origin of the excellent properties will be discussed. [DOI: 10.1380/ejsnt.2009.791]

Keywords: Mg hydroxide; Carbon; Optically transparency; Electric conductivity; Sputter deposition

I. INTRODUCTION

Indium oxide doped with Tin oxide, ITO has been widely used as a key material for liquid crystal display technologies because of its high transparency and electro conductivity. Recently, however, its high cost due to the scarcity (Clarke number is 10^{-5}) and the toxics of indium oxides have been strongly pointed out so that alternative transparent and electro conductive materials have been actively studied over the last two decades [1–4].

Our research group has studied on synthesizing Mg based alloys by Mechanical Alloying (MA) and their properties, i.e., hydrogen solubility in the non-equilibrium and/or meta-stable phases [5–7]. From series of our works, it has been demonstrated that even immiscible elemental couples could be alloyed by accumulating the excess mechanical energy created during MA process. In fact, Mg-C couple is the case [8]. According to equilibrium phase diagram which is drawn by calculation semi-empirical method, existence of MgC intermetallic compound was expected [9].

In this study, Mg-C compound was first synthesized by co-sputtering method because the significant large excess energy could be expected during process which could reach even several hundred of kJ/mol. This energy might be high enough to compensate the large positive mixing enthalpy for Mg-C couple.

We will propose newly developed compound composed of elements of Mg-C-O-H with the potential high transparency and electro conductivity. In order to obtain the transparency without losing electro conductivity, the material was synthesized with two different steps including alloying of Mg-C by magnetron co-sputtering and post-reaction of the film with moisture in the air. It was found that the compound has a Brucite type hexagonal structure of $\text{Mg}(\text{OH})_2\text{-C}$. From our literature survey, it was concluded that transparent conductive materials are

FIG. 1: Change in appearances of sputtered $\text{Mg}_{80}\text{-C}_{20}$ composite films. (a) As-sputtered film and (b) transparent film.

FIG. 2: SEM images of the $\text{Mg}(\text{OH})_2\text{-C}$ transparent film. (a) Surface and (b) cross section.

metal oxides without exception. In this paper the transparent and electro conductive properties of non-oxide material, $\text{Mg}(\text{OH})_2\text{-C}$ will be demonstrated.

II. EXPERIMENTAL PROCEDURES

The Mg-C films were fabricated on glass substrates ($25 \times 25 \text{ mm}$, Corning Inc. #1737) in the Ar atmosphere (0.5 Pa) with the electrode using an rf-magnetron sputtering method (ANELVA, SPC-350). In this work, Mg (99.9% of purity, 76.2 mm in diameter) and Carbon (99.9% of purity, 76.2 mm in diameter) targets were used. The target was placed on the each cathode with the magnetron. The sputtering chamber was evacuated to reach 10^{-4} Pa of pressure and then Ar was introduced. The electric power density applied to the cathode was a closely controlled at $23\text{--}26 \text{ kW/m}^2$ and 100 kW/m^2 for Mg and

* This paper was presented at International Symposium on Surface Science and Nanotechnology (ISSS-5), Waseda University, Japan, 9-13 November, 2008.

†Corresponding author: tkuji@wing.ncc.u-tokai.ac.jp

FIG. 3: X-ray diffraction patterns for as-sputtered film, Carbon, Mg, Mg-C and the Mg(OH)₂-C transparent films.

carbon, respectively. The duration of the deposition was 3600 sec in this work. Substrate holder was revolved at speed of 60 r/m. Temperature in the chamber was 297-330 K and substrate temperature was not controlled. In fact, substrate temperature did not increased significantly. Before sputtering Mg and C, four Ag electrodes were prepared in parallel on the glass substrate by sputtering for measuring the electric resistance of the films. Prepared Mg-C films were exposed into the air, i.e. 298 K and 40% of humidity for 3 Ksec. The electric conductive measurement was carried out by the four terminal methods as explained above.

A crystallographic structure and a surface morphology of Mg-C thin film samples were identified by an X-ray diffraction analysis method (PHILIPS, X'Pert-MRD), operating at 40 kV and 40 mA of Cu_{kα}, scanning electron microscope (HITACHI, FE-SEM S-4000), respectively. After synthesized of the sample on the FIB machine (HITACHI, FB-2000A), the transmission electron microscopy (TEM) analysis were determined by using the high resolution TEM (HITACHI, FE-TEM HF 2200TV), operating at 200 kV. The elemental concentrations and operation condition in the films were analyzed by an X-ray photoelectron spectroscopy (ULVAC-PHI Inc., Quantum 2000-TK) and the wavelength dispersive X-ray analysis. Electrical resistivity was measured by 4-terminal d.c. method (HIOKI, LCR HITESTER 3522), operating at 1 mA. Optical transmission through the film was measured by ultraviolet/visible/NIR spectrophotometer (JASCO, V-570), 350 to 1000 nm.

III. RESULTS AND DISCUSSIONS

Figure 1 shows an appearance of as-sputtered Mg₈₀-C₂₀ film and the same film after exposing in the air. We can see excellent and clear transparency after exposing in the air at 298K and 40% of humidity. We can see clearly our

FIG. 4: From the XRD pole figure measurements for the (001) and (101) peaks of the samples.

FIG. 5: HTEM image of the Mg(OH)₂-C transparent film.

FIG. 6: Depth profile of X-ray photoelectron spectroscopy of the Mg(OH)₂-C transparent film.

FIG. 7: Element mapping of the $\text{Mg}(\text{OH})_2\text{-C}$ transparent film. FIG. 8: Hypothetical lattice model of $\text{Mg}(\text{OH})_2\text{-C}$.

university logo placed behind the $\text{Mg}(\text{OH})_2\text{-C}$ film and glass substrate. In order to confirm this behavior, N_2 , O_2 or dry air was introduced into the sputtering chamber immediately after sputtering. However, no transparency appeared in any cases even after 17.3 ks [10]. Figure 2 shows the (a) surface morphology and (b) the cross section of the transparent film. We can see the granular surface with size of approximately 100 nm and the film thickness was thicker than 2 μm . Figure 3 shows XRD patterns from sputtered Carbon, Mg, as-sputtered Mg-C and the transparent films. It should be noted here that as-sputtered Mg-C film showed a diffraction peak which was not able to be identified with peaks from either C or Mg. Moreover, it was not identified with MgC_2 (JSPDS, 03-0748) and Mg_2C_3 (JSPDS, 47-1456). From the above results, it is believed that a new Mg-C crystalline phase appeared in the study, although it has not been determined crystal symmetry due to the information from the narrow diffraction angles [11]. As mentioned previously, after exposing the Mg-C black-gray film in the air, the film became transparent. From the diffraction peaks of the transparent film, the transparent film had a hexagonal $\text{Mg}(\text{OH})_2$ lattice symmetry and lattice was slightly elongated along the hexagonal c-axis [12] compared with $\text{Mg}(\text{OH})_2$ due to the existence of C in $\text{Mg}(\text{OH})_2$ lattice discussed later. From the XRD pole figure measurements for the (001) and (101) peaks distributions as shown in Fig. 4, it can be concluded that the $\text{Mg}(\text{OH})_2\text{-C}$ grains are preferentially aligned in hexagonal $\text{Mg}(\text{OH})_2$ c-axis. This could be confirmed easily compared to the results from $\text{Mg}(\text{OH})_2$ powders. This result seems to expect the anisotropy of the transparency and electric conductivity, which is our future work we should do. The lattice image from HTEM indicates crystalline size is more and less 5

FIG. 9: Optical transmittance spectra of the $\text{Mg}(\text{OH})_2\text{-C}$ film.

nm, as shown with dotted circle.

Let's think on the two-step process to synthesize $\text{Mg}(\text{OH})_2\text{-C}$ compound. The process can be estimated as below:

The interest characteristics of the above both reactions are that are exothermic. In general, exchange reaction is composed of exothermic and endothermic process. It is of important to say that that C is exchanged from Mg-C to $\text{Mg}(\text{OH})_2\text{-C}$ according the above reactions (1) and (2). However, in this work C was not segregated but stayed in $\text{Mg}(\text{OH})_2$ structure as mentioned below. HTEM, XPS shown in Fig. 5 and Fig. 6, respectively and EPMA elemental mapping for Mg, O and C shown in Fig. 7 did not show any evidence of C segregation in the film morphology from the above estimation on the reactions (1) and (2). Moreover, XPS indicated that Mg and C composition in the film was almost same as expected and Mg/C ratio does not vary from the surface to the deep inside of the film. Hypothetical model of the $\text{Mg}(\text{OH})_2\text{-C}$ lattice is shown in Fig. 8. In this case half of H atoms are replace

FIG. 10: Resistivity of the $\text{Mg}(\text{OH})_2\text{-C}$ transparent film.

by C atoms, which could be the possible case from our Rietveld's analysis [13]. This estimation of the C position in the $\text{Mg}(\text{OH})_2$ lattice structure seems to be confirmed by XPS for C. The spectrum for C showed the existence of the C-O bonds. As well known, there are different peaks corresponding different types of C-O bonds in the narrow energy range. However, at least the above XPS spectrum result is well consistent with Rietveld's analysis based upon replacement of H by C. We have a plan to do the work focused on the C position of $\text{Mg}(\text{OH})_2$ lattice structure.

From the above, it can be concluded that the reaction of Mg-C with moisture in the air yielded the transparency of the film. Figure 9 shows the optical transmittance of the film with wavelength. It can be seen that the optical transmittance of the film is $>90\%$ for the visible light (380-780 nm), which is excellent even compared with practical ITO.

Figure 10 shows the electric resistance of the transpar-

ent films. The resistance of as-sputtered MgC black film increased with losing the color gradually after exposing it in the air [10, 12]. Then the variation in resistance somewhat flat with time when the film became almost completely transparent, although degrading still exists with time. The resistivity is strongly dependent upon the C composition in the film as shown in Fig. 10. The electric resistivity of the $\text{Mg}_{60}\text{C}_{40}$ transparent film was of the order of $10^{-2} \Omega\text{cm}$. For practical uses, we need one order lower value of resistivity of the film, which is $10^{-3} \Omega\text{cm}$, which is an important present work made effort in our group because of opening wide applications for our $\text{Mg}(\text{OH})_2\text{-C}$ film.

IV. CONCLUSIONS

In this work, Mg-C crystalline phase was successively prepared by co-sputtering of Mg and C. The synthesized phase was not identified any phase previously reported in the literature. So we believe the Mg-C phase seems to be a new phase for the Mg-C system, although it might be non- or meta-stable phase.

The Mg-C black film became transparent with time after air exposing for appropriate time. This transparency behavior was yielded by the reaction of Mg-C with moisture in the air. Consequently, the film was composed with nano-sized grains with the lattice symmetry of $\text{Mg}(\text{OH})_2$. This film had excellent optical transmittance for the visible light and again excellent low electric resistance of the order of $10^{-2} \Omega\text{cm}$.

In conclusion we could successively develop new transparent conductor of $\text{Mg}(\text{OH})_2\text{-C}$.

Acknowledgments

Authors would like to thank Prof. Shibuya for the help during the optical transmittance analysis in Tokai University. Mr. Miyamoto and Mr. Haraki are acknowledged for their support structure analysis.

- [1] The 166th Committee on Photonic and Electronic Oxide, JSPS, *Toumeidoudenmaku no gijyutu* (in Japanese) (Ohmsha, Ltd., 2007).
- [2] K. Ellmer, R. Cebulla, and R. Wendt, *Thin Solid Films* **317**, 413 (1998).
- [3] K. Hayashi, K. Kondo, K. Murai, T. Moriga, I. Nakabayashi, H. Fukumoto, and K. Tominaga, *Vacuum* **74**, 607 (2004).
- [4] T. Minami, *Ionics* **97** (1989).
- [5] J.-C. Crivello, T. Nobuki, S. Kato, M. Abe, and T. Kuji, *J. Alloys Comp.* **446-447**, 157 (2007).
- [6] T. Nobuki and T. Kuji, *J. Adv. Sci.* **19**, 11 (2007).
- [7] M. Abe, and T. Kuji, *J. Alloys Comp.* **446-447**, 200 (2007).
- [8] T. Honjo, T. Nobuki, M. Chiba, and T. Kuji, *J. Japan Inst. Metals* **71**, 603 (2007).
- [9] T. N. Legkaya, *Soviet J. Superhard Mater.* **12**, 1 (1990).
- [10] T. Honjo, M. Chiba, T. Nobuki, and T. Kuji, *Hyomen Kagaku* **29**, 532 (2008) (in Japanese).
- [11] T. Honjo, T. Nobuki, and T. Kuji, *J. Japan Inst. Metals* **72**, 780 (2008).
- [12] T. Kuji, T. Honjo, M. Chiba, T. Nobuki, and J.-C. Crivello, *e-J. Surf. Sci. Nanotech.* **6**, 15 (2008).
- [13] T. Honjo, J.-C. Crivello, and T. Kuji, *J. Alloys Comp.* to be published.