



# Electronic structure of chromium-containing amorphous hydrogenated carbon thin films studied by X-ray absorption spectroscopy

Hsin-Yen Cheng<sup>a</sup>, Jau-Wern Chiou<sup>b</sup>, Jyh-Ming Ting<sup>a,\*</sup>, Jin-Ming Chen<sup>c</sup>, Jyh-Fu Lee<sup>c</sup>, Yonhua Tzeng<sup>d</sup>

<sup>a</sup> Department of Materials Science and Engineering, National Cheng Kung University, Tainan 701, Taiwan

<sup>b</sup> Department of Applied Physics, National University of Kaohsiung, Kaohsiung 811, Taiwan

<sup>c</sup> National Synchrotron Radiation Research Center, Hsinchu 300, Taiwan

<sup>d</sup> Department of Electrical Engineering, National Cheng Kung University, Tainan 701, Taiwan

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## ABSTRACT

C K-, Cr L<sub>3,2</sub>-, and K-edge X-ray absorption near-edge structure (XANES) analysis, high-resolution transmission electron microscopy examination, and optical absorptance have been examined to obtain a correlation between the optical absorptance and electronic structure of chromium-containing amorphous hydrogenated carbon thin films (a-C:H/Cr) deposited using a dc magnetron sputter deposition technique. It was found that the C 2p–Cr 3d hybridization gradually increases as the Cr nanoparticle (NP) size decreases, accompanied by a C 2p interband transition. The amount of C–H bonding and the change in crystalline structure are the main factors affecting the optical absorptance of the thin films. The size of the Cr NP affects the absorption wavelength range of the films. The optical absorptance and C K-edge XANES spectra indicate that a decrease in the size of Cr NP raises the conduction-band-minimum and may also increase the bandgap.

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## 1. Introduction

In recent years, growing concerns have been paid to alternative energies such that tremendous amounts of researches are being undertaken to explore the use of solar radiations. Solar radiations can be converted into a usable form of energy as heat or electricity. For the conversion into heat, thin films are used as the coatings on selective solar absorbers. An ideal coating for solar absorbers is required to exhibit high solar absorptance ( $\alpha$ ) and low thermal emittance ( $\varepsilon$ ) [1,2]. Various films have been investigated to meet such a requirement. One type of the thin films consists of a single material. For example, a copper oxide thin film prepared using a one-step chemical conversion method exhibited an  $\alpha$  and an  $\varepsilon$  of 0.94 and 0.08, respectively [3]. Of particular interest for solar absorber coatings is thin films consisting of a metal and a dielectric material. Several material combinations have been used in this type of thin films.

Titanium-containing amorphous hydrogenated carbon thin films (a-C:H/Ti) deposited on an Al substrate using a combined physical vapor deposition and plasma enhanced chemical vapor deposition process was found to exhibit an  $\alpha$  of 0.876 and

an  $\varepsilon$  of 0.061 at 100 °C [4]. Layered cermet structure of molybdenum–aluminum oxide (Mo–Al<sub>2</sub>O<sub>3</sub>) thin films deposited on copper and thin glass substrates by DC reactive magnetron sputter deposition exhibit an  $\alpha$  of 94% and an  $\varepsilon$  of 5% at room temperature [5]. Mo/Mo–SiO<sub>2</sub>/SiO<sub>2</sub> thin films with a  $\alpha$  of 0.95, a low  $\varepsilon$  of 0.097 at 353 K, and high thermal stability were obtained using DC and RF co-sputter deposition [6]. Three-layer absorbers consisting of a top anti-reflection hydrogenated amorphous carbon, a middle layer chromium-containing amorphous hydrogenated carbon (a-C:H/Cr) thin film, and a bottom layer of Cr–C deposited on Cu substrates using combined plasma activated chemical vapor deposition and magnetron sputter deposition give an  $\alpha$  and an  $\varepsilon$  of 0.918 and 0.086, respectively [7]. During deposition the substrate was heated to 300 °C and a DC-biased (–200 or –600 V) were used.

In this study, we have investigated chromium-containing amorphous hydrogenated carbon thin films for not only the optical performance using spectrophotometry and Fourier transform infrared (FTIR) spectroscopy but also the electronic structures using X-ray absorption spectroscopy (XANEX). The optical performance of a-C:H/Cr thin films has been studied [7,8]. However, the information of the electronic structures studied using XANEX has been missing but is of great significance. XANES analysis represents a useful and unique technique to examine the electronic structure of thin films. For example the electronic structure of Al-doped ZnO thin films and the Cr secondary oxide phases in ZnO films have

\* Corresponding author. Tel.: +886 6 2757575x62949; fax: +886 6 2385613.  
E-mail address: [jting@mail.ncku.edu.tw](mailto:jting@mail.ncku.edu.tw) (J.-M. Ting).

been investigated using XANES technique [9,10]. The relationship among the crystalline structure, optical absorbance, and electronic structure is discussed.

## 2. Experimental

a-C:H/Cr thin films were deposited on oxygen-free copper (OFC) and Si substrates using dc magnetron sputter deposition. A 3-inch Cr (99.99%) was used as the target. Pre-sputtering was performed under an Ar pressure of 1.3 Pa ( $1 \times 10^{-2}$  Torr), a dc power of 100 W, and a working distance of 50 mm for 3 min. The sputtering gas was a mixture of methane and argon. In one group of experiments, the volumetric concentration of methane was fixed at 10%, 20%, and 30%, and the resulting samples are designated as 10%, 20%, and 30% thin films. In the other group of experiments, the volumetric concentration of methane was varied from 0 to 30% at an interval of 10% throughout the deposition period. The resulting samples are designated as VM thin film. When the methane concentration was varied from 0% to 30%, the pre-determined deposition times at 0%, 10%, 20%, and 30% were 40, 70, 70, and 70 s, respectively. During all the deposition conditions, the substrates were not heated and no substrate bias voltage was applied.

The optical absorbance spectra of the samples were measured in the wavelength range between 0.2 and 2.5  $\mu\text{m}$  using Perkin Elmer Lambda 950 spectrophotometry with an integrating sphere (0.15 m diameter) at AM 1.5. The near-normal infrared reflectance spectra of the samples were measured in the wavelength range between 2.5 and 15  $\mu\text{m}$  using Perkin Elmer FTIR spectroscopy. The microstructure was investigated using field emission transmission electron microscopy (FE-TEM). C *K*-, Cr *L*<sub>3,2</sub>-, and *K*-edge XANES spectra were obtained at the National Synchrotron Radiation Research Center in Hsinchu, Taiwan. Both thermal and humidity cycling were performed following the methods described elsewhere [11,12]. Thermal cycling test was performed using a thermal shock chambers under the temperature range of  $-65^\circ\text{C}$  to  $150^\circ\text{C}$  and air to air. The dwell times at both temperatures were 30 min and the number of cycles was 50. Humidity test was also performed using the thermostatically controlled humidity chamber. The relative humidity (RH) was carried from 10% to 98% in 48 h at  $50 \pm 1^\circ\text{C}$ . The C *K*- and Cr *L*<sub>3,2</sub>-edge XANES spectra were measured in the total electron yield by using a high-energy spherical grating monochromator beamline. For all the samples, the Cr *K*-edge XANES spectra were obtained from a wiggler beamline by using the total fluorescence yield method. The incident beam was perpendicular to the sample's surface. The typical resolution of the C *K*- and Cr *L*<sub>3,2</sub>-edge XANES spectra was set to 0.1–0.2 eV at a photon energy of 280–600 eV, whereas the resolution of the Cr *K*-edge XANES spectra was set to 0.3 eV at a photon energy of 5900–6100 eV during measurements.

## 3. Results and discussion

The thicknesses of the 10%, 20%, 30%, and VM a-C:H/Cr thin films deposited on Si were determined to be 165, 228, 137, and 145.5 nm, respectively. The Cr concentrations of the 10%, 20%, and 30% thin films are 74.2%, 37.0%, 12.8%, respectively. The Cr concentration decreases with the methane concentration. These a-C:H/Cr thin film exhibit similar structures in which Cr nanoparticles (NPs) are embedded in an amorphous carbon matrix. The Cr NP size decreases with the methane concentration. The particle sizes of the 10%, 20%, and 30% thin films are 22, 10, and 5 nm, respectively. It was also found that the crystallinity of the Cr NP decreases with the size. The Cr NPs are crystalline in the 10% thin film and amorphous in the 30% thin film. The Cr NPs in the 20% thin film exhibit poor crystallinity. For the VM thin film, as shown in Fig. 1, there are different regions

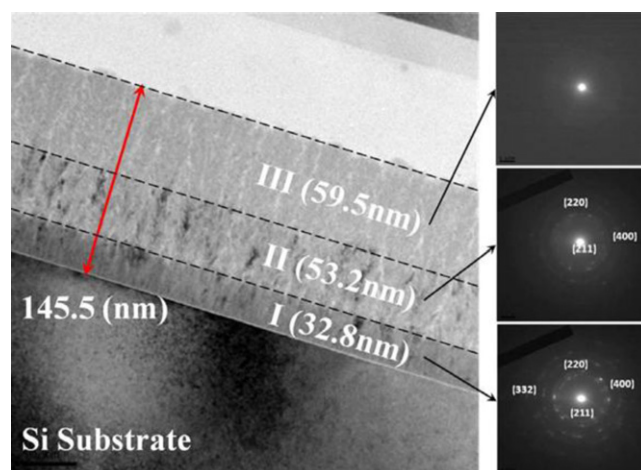


Fig. 1. HR-TEM image and its corresponding electron diffraction patterns of the VM thin film.

because of the varying methane concentrations during deposition. Layers I, II, and III were obtained while the methane concentration was varied from 0 to 10, 10 to 20, and 20 to 30%, respectively. Layers I, II, and III have thicknesses of 32.8, 53.2, and 59.5 nm, and Cr atomic concentrations of 66, 28, and 6, respectively. The selected area diffraction (SAD) patterns of Layers I and II show the existent of crystalline Cr. However, no diffraction pattern was observed in Layer III, indicating that the crystalline structure is amorphous. The Cr NP sizes in Layers I, II and III are in the range of 2.6–6.7 nm, 2.7–4.2 nm and 1.1–1.8 nm, respectively.

Fig. 2 shows the optical absorbance of the a-C:H/Cr thin films, and the reference 190-nm thick pure Cr and 200-nm thick amorphous C (a-C) thin films, in the wavelength region of 0.2–2.5  $\mu\text{m}$ . These films were deposited on Cu. Optical absorbance of the reference a-C thin film is primarily at the UV to visible region (0.2–0.6  $\mu\text{m}$ ). The optical absorbance of the a-C:H/Cr thin films obtained at fixed methane concentrations are reduced due to the addition of Cr. The optical absorbance of a-C:H/Cr thin film decreases with the Cr concentration or Cr NP size in the 0.2–0.6  $\mu\text{m}$  region. The optical absorbance of the reference pure Cr thin film appears to define the lower bonding in this region. Meanwhile, with the decreasing Cr concentration the peak absorbance shifts to a longer wavelength, approaching to that of the pure a-C thin

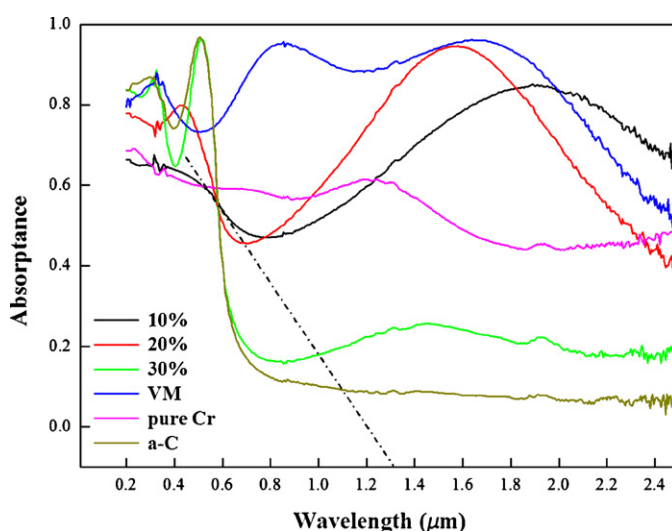


Fig. 2. Optical absorbance of various a-CH/Cr thin films, and reference pure Cr and a-C thin films.

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