Optical Detection of Carbon Dioxide Adsorption on Epitaxial CuFe_{1-x}Ga_xO₂ Delafossite Film grown by Pulse Laser Deposition

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Abstract:

A highly epitaxial Delafossite CuFe_{1-x}Ga_xO₂ film was made with Pulse Laser Deposition in high vacuum. The sample thickness was around 48 nm and it was terminated with CuFeO₂. This Delafossite sample was exposed to a CO₂ atmosphere under controlled conditions and chemisorption of CO₂ on the surface was observed. Transmittance and Reflectance spectroscopy were recorded for the sample post surface heat treatment held in a vacuum chamber (0.05Kpa) and after exposure to CO₂. Both spectra were recorded over a wavelength range of 350nm-1100nm. Chemisorption of CO₂ was correlated with an increase in transmittance and decrease in reflectance in the pressure range 0-60 kPa. These observations were confirmed with X-Ray photoelectron spectroscopy and thermal programmed desorption data obtained in an independent experiment. The CO₂ is bound to the surface forming a carboxylate structure via coordination of a bent CO₂^{-δ} molecule to a Cu center .

1. Introduction

There is an increasing worldwide concern about developing new sources of energy other than burning oil or coal [1-4]. This is due to near future shortage of oil reserves and also to the environmental problems associated with carbon dioxide production. Attractive alternatives are production of hydrogen from water splitting or being able to do carbon dioxide reforming. Water dissociation can be explored in a similar way as that of the electrochemical water photolysis experiments by Honda et al in 1972 [5] but using alternative materials to make photoelectrodes. Honda described the electrochemical decomposition of water using TiO_2 as a photoelectrode and the decomposition was achieved with a potential difference of no more than 1.23 V between electrodes. If light energy is used effectively in this system by finding an appropriate material, it would be possible to reach electrochemical water decomposition using most of the visible part of the sun spectrum. The search for a semiconductor material with a band gap near the water splitting potential has been the goal of many researchers who work within this field [6]. One prior step to understanding any heterogeneous catalyzed reaction is to study and learn about the adsorption of H_2O or CO_2 by these new materials.

A very promising class of materials is the family derived from Delafossite oxide [7]. This oxide family displays a wide band gap semiconductor behavior capable of absorbing UV, visible and near infrared light. As with more common semiconductor materials the band gap(s) can be adjusted by changing the composition of the oxide.

In the present work, we made a multilayer film by alternating monolayers of CuFeO_2 with CuGaO_2 . We wished that the film made in such a manner would have different electronic properties, reflected in a modified semiconductor band gap, and that this would impact on the surface adsorption of gases such as water and CO_2 . The technical feasibility in using these Delafossite oxides as photo-conducting electrodes relied on the successful fabrication of thin films of these materials. Obtaining thin films with very good properties (good stoichiometry and low surface roughness) was one of the main goals in this study. A rapid screening optical technique that would allow us to detect CO_2 chemisorption on different materials was another important goal in this study.

The reasons why we focused on the study of CO_2 chemisorption on Cu containing Delafossite oxides are the following:

A) The crystallographic structure of the Delafossite oxide, a mineral discovered by the crystallographer G. Delafosse, was revealed and first reported by Friedel in 1873 [7] as a natural copper and iron oxide of the formula CuFeO_2 . In 1935 it was synthesized for the first time by Pabst et al [8] via solid state synthesis. Later, composition variations of these oxides created an all-new family of materials that share the crystal structures with similar properties, permitting many different applications [9]. The Delafossite oxide family has a general chemical formula AMO_2 where A is a monovalent cation and M is a trivalent metal from Al to La [10]. By varying their stoichiometric chemical composition (changing the M elements used) it is possible to form p-type or n-type semiconductors [11-14]. An additional

43 advantage of these complex oxides is the relative abundance of their main composite
44 materials in the form of Cu, Fe, Al, Ga, etc.

45 B) The adsorption behavior of the multilayer film containing Cu would be suitable for
46 carbon dioxide reforming because Cu-based catalysts are known to perform very well in the
47 methanol synthesis [15]. It is generally accepted that CO₂ is adsorbed well by oxide
48 surfaces. We have studied the adsorption of CO₂ on different ferroelectric materials with a
49 Perovskite structure [16]. Carbon dioxide chemisorbs well on other oxide surfaces [17] and
50 it is also known that CO₂ adsorbs in two states, a molecular bent CO₂^{-δ} state and dissociated
51 states [18].

52
53 One problem associated with the synthesis of Delafossite oxides in films is obtaining the
54 right stoichiometry. The reaction of stoichiometric amounts of Cu oxide and Fe oxide to
55 produce CuFeO₂ rather favor the formation of CuFe₂O₄, an oxide lacking the desired
56 semiconducting properties. We were successful in obtaining highly epitaxial CuFeO₂
57 Delafossite Oxides by Pulse Laser Deposition (PLD) [19] which encouraged us to attempt
58 to modify CuFeO₂ with Ga in order to modify its band gap and thus the adsorption
59 properties.

60
61 In this work we report the successful fabrication of a highly epitaxial Delafossite
62 CuFe_{0.75}Ga_{0.25}O₂ film and the remarkable observation of CO₂ adsorption on this film using
63 IR/visible transmittance and reflectance spectroscopy. These observations are confirmed by
64 thermal programmed desorption measurements in an ultra-high vacuum system (UHV) and

surface composition before and after adsorption analyzed by X-ray photoelectron spectroscopy. The Delafossite film was characterized by XRD, Raman and band gap measurement.

2. Experimental

2.1 Film of CuFeO₂/CuGaO₂

CuFeO₂ (001) films were deposited onto Al₂O₃ (001) substrates from a stoichiometric polycrystalline CuFeO₂ target using pulsed laser deposition. Further details about the experimental setup and procedure have been described elsewhere [19]. In order to make the multilayer structure, a buffer layer of 9 monolayers of CuFeO₂ was grown on top of the sapphire substrate. Then one monolayer of CuGaO₂ was deposited on top, followed by three monolayers of CuFeO₂. This CuGaO₂/CuFeO₂ was repeated 21 times. Thus the surface was terminated by CuFeO₂. The film was grown in a vacuum system at 600°C under an O₂ partial pressure of 1.33×10^{-2} Pa.

2.2 Characterization Film of CuFeO₂/CuGaO₂

a. XRD

A four-axis Rigaku x-ray diffraction (XRD) system with a Cu K_α rotating anode and Huber goniometers was used for structural characterization of the deposited films. CuFeO₂ and

CuFe₂O₄ phases were identified using powder diffraction files # 01-075-2146 and #00-025-0283, respectively.

b. Raman spectroscopy

Raman spectra were obtained using a LabRam010 system from Instruments, S.A. (Horiba), featuring a 5.5 mW He–Ne laser (632.8 nm wavelength). This instrument used an Olympus confocal optical microscope with a light spectrometer in a back-scattering geometry, where the incident beam was linearly polarized and spectral detection was unpolarized. The spectra were taken at room temperature using a 100X objective (~10 µm spot size) with an energy resolution of approximately 1 cm⁻¹.

c. Optical Properties

Transmittance and Reflectance spectroscopy were recorded for the sample post surface heat treatment. A description of the experimental apparatus can be found elsewhere [20]. Both spectra were recorded over wavelength range 350nm-1100nm corresponding to photon energies 1.12eV - 3.5eV. The sample was held in a vacuum chamber (0.05Kpa) post heat treatment to avoid oxidation and other surface adsorbance reactions. The chamber pressure was varied between 0-90 kPa using a pure source of pressurised CO₂. Transmittance and reflectance spectra were recorded over the described range at each interval of pressure. Analysis of the correlation between optical spectra and CO₂ chamber pressure was performed by the integration of the entire spectral signal at each interval. By this method

the samples' reaction to increased pressure could be observed. No correlation was found between integrated transmittance and CO₂ pressure when: (i) the chamber contained no sample (purely a test for relative transmittance with respect to CO₂ pressure) (ii) the chamber contained a control sample of Al₂O₃ (001) substrate, assumed to be chemically inert with respect to CO₂ (iii) the chamber contained the composite layer sample prior to heat treatment for surface oxidation and the removal of impurities.

2.3 CO₂ Adsorption

a) *X-Ray photoelectron spectroscopy*

The surface chemical information was obtained by X-Ray photoelectron spectroscopy (XPS) before and after the sample was exposed to CO₂ injection. Measurements were performed with a STAIB RQ300X X-Ray source using Mg K_α x-radiation and a STAIB DESA100 electron spectrometer as detector, which was operated in a constant pass energy mode at 225W. The working pressure in the analysis chamber was typically 6x10⁻⁷ Pa. The binding energy scale was calibrated by measuring the C 1s peak at 284.8 eV. The composition and chemical state were investigated on the basis of the areas and binding energies of O 1s, C 1s, Fe 2p and Cu 2p photoelectron peaks and Cu (L₃VV) Auger peaks. Data analysis was performed by a fitting program using properly mixed Lorentzian-Gaussian functions after background subtraction according to the Shirley method. Surface atomic compositions were determined using standard XPS cross sections.

b) *Thermal Programmed Desorption (TPD)*

The film over the sapphire substrate was placed on an all stainless steel UHV chamber from MDC-Vacuum Inc. which has a volume of approximately $4 \times 10^{-2} \text{ m}^3$ and is pumped by an Adixen $0.15 \text{ m}^3/\text{s}$ Turbo pump, backed by a rotary pump. This apparatus was used for all of the CO_2 TPD experiments. The UHV system incorporated an x-ray source (STAIB RQ300X), a double-pass cylindrical mirror analyzer system (DESA 100) from Staib Instruments, a mass spectrometer (RGA 200) from Stanford Research Systems and Ar^+ sputtering ion source (IQE 11/35) from Specs. A home-built manipulator was used to perform the TPD experiments. The manipulator was mounted on a rotary feed-through from the MDC-Vacuum which had two degrees of freedom of motion: rotation over 360° was possible, alongside translational motion up and down over a range of $2.54 \times 10^{-2} \text{ m}$. Two rigid Cu bars, $0.635 \times 10^{-2} \text{ m}$ in diameter were used for heating the sample foils via electrical resistance. The bars were supported by a piece of Macor ceramic. The sample was fixed to the Macor ceramic using stainless steel foil with screws, a chrome-alumel thermocouple was soldered to the stainless steel foil to feed back the temperature controller (Eurotherm 2404). The gas dosage was done through an MDC leak valve connected to the vacuum system and using 99.9 % pure CO_2 . The main impurity in the CO_2 was water.

3. Results

XRD done to the film, displayed in Figure 1, shows that the film is mainly a Delafossite structure with some formation of spinel (CuFe_2O_4) impurities. The film is mainly oriented in the $[00.1]$ direction displaying a c lattice constant of 1.7095 nm, smaller than a pure

CuFeO₂ film (1.728 nm) grown under similar conditions [19]. The rocking curve obtained (Figure inserted in Fig. 1) shows that there is no super-lattice structure. The film obtained is a solid solution with a composition of CuFe_{1-x}Ga_xO₂ and Delafossite structure. The Ga content in the solid solution could in principle be determined by the c and a lattice parameter since the primitive cell volume in the bulk linearly decreases with Ga content in the solution [21]. Unfortunately, our films grew under stress due to the lattice mismatching with the substrate yielding a larger c parameter than the bulk parameter. Counting the monolayer deposited during the growth process we can estimate that the Ga content is 25 at. %.

3.1 Raman spectroscopy

Raman spectra acquired for the sample is shown in Figure 2. This spectra shows three main characteristic peaks at 363, 521, and 700 cm⁻¹. A pure CuFeO₂ film has three peaks at 350, 511 and 689 cm⁻¹ [19] whose positions and relative magnitudes were consistent with other reported CuFeO₂ materials [22 - 24]. In the case of CuFeO₂, the vibrational mode at 350 cm⁻¹ was attributed to the E_g mode along the c axis of the octahedral structure. The peak located at 689 cm⁻¹ was attributed to the A_{1g} vibrational mode along a perpendicular plane to the c axis. The peak found at 511 cm⁻¹ was attributed to non-zero wave vector phonons typical of crystalline defects [23]. Consequently, the peaks seen in the case of our sample of CuFe_{1-x}Ga_xO₂ at 363, 521, and 700 cm⁻¹ correspond to the same modes but shifted 16 cm⁻¹ due to the inclusion of Ga in the solid solution. A pure CuGaO₂ sample shows Raman peaks

at 368 and 729 cm⁻¹ [24]. Assuming that the Raman peaks shift to higher values linearly with Ga content, we can determine that the Ga is at 25-40 atom % in the solution.

3.2 Optical band Gap

The results for optical transmittance were treated in order to determine the possible band gap energies (E_g) of the sample using Tauc's expression [25]:

$$\alpha h\nu = b (h\nu - E_g)^{1/2} \quad \text{Equation (1)}$$

where h is the plank constant, ν is the frequency of the incident light, α is the absorption coefficient, b is a proportion constant and E_g is the band gap energy defined as the difference between the lowest energy level in conduction band and the highest energy level in valence band. Where linearity was identified within the Tauc plot, extrapolation to the x axis revealed possible optical band gap energies for the sample. The process was repeated, once using power 2 so as to identify direct gap behavior, and secondly using power $\frac{1}{2}$ to identify behavior characteristic of indirect energy gaps within the layer [25].

The Tauc plot is shown in Figure 3a, the possible direct energy gaps recorded from this composite material sample were found at 2.4 eV, 2.8eV and 3.1eV (+0.1eV). The results for possible indirect gap transitions were found at 0.9 eV and 1.3 eV (+0.1eV) and shown in Figure 3b. These results were found in agreement with reports of energy gap studies for CuFeO₂ thin films [19], and also we expected that the presence of the Ga in the solid

189 solution would modify the energy gap results. We observe a multiplicity of characteristic
190 linear regions within the Tauc plots corresponding to both direct and indirect energy gaps.

192 ***3.3 Optical properties under CO₂ exposure***

193 The sample was flash desorbed in order to remove residual gases from the surface. After
194 this desorption, the CuFe_{1-x}Ga_xO₂ sample showed a strong positive correlation between
195 integrated transmittance and CO₂ pressure within the chamber. The peak transmittance
196 varied to a much lower degree than the integrated transmittance, indicating a heterogeneous
197 change in surface optical properties across the spectra. The principal change in
198 transmittance could be observed over the interval 600nm-900nm corresponding to the peak
199 response of the Si photodiode. Conversely, after the surface heat treatment cycle was
200 repeated, the sample showed a strong negative correlation between reflectance and CO₂
201 pressure.

203 A plot of the normalized transmittance and reflectance is shown in Figure 4. The
204 normalized transmittance is calculated with the formula:

$$\frac{\Delta T}{T} = \frac{T_{CO_2} - T_0}{T_0} \quad \text{Equation (2)}$$

206 Where T_0 is the integrated transmittance of the sample under vacuum and T_{CO_2} is the
207 integrated transmittance of the sample exposed to CO₂ pressure.

208 The normalized reflectance is calculated in the same manner:

$$\frac{\Delta R}{R} = \frac{R_{CO_2} - R_0}{R_0} \quad \text{Equation (3)}$$

210

211 From this consistency between normalized transmittance and reflectance we inferred that
 212 the surface optical characteristics had changed during the chamber pressurisation with CO₂.
 213 These results were highly suggestive of surface chemical adsorption of CO₂ by the thin film
 214 material, causing the sample reflectivity to decrease, and hence resulting in increased
 215 transmittance. Reflectance is more surface sensitive than transmittance and so the
 216 transmittance shows more significant scatter in the data.

217

218 ***3.4 X-Ray photoelectron spectroscopy***

219 The XPS spectra of the sample before CO₂ exposure was measured. The spectrum for Cu
 220 2p displayed in Figure 5 (a) shows that the dominant binding energy corresponds to Cu¹⁺
 221 oxide [26 - 28] . The absence of satellite peaks and the position of the Cu (L₃VV) Auger
 222 peak at 916.2 eV, confirmed this chemical state.

223 The Fe 2p spectrum is shown in Figure 5 (b). In this plot it was possible to observe
 224 binding energies corresponding to Fe³⁺ oxide [29, 30], as the most abundant and some Fe²⁺
 225 oxide [31]. This result agreed well with the chemical configuration for CuFeO₂ Delafossite
 226 reported [32].

227 The XPS spectra of Cu 2p and Fe 2p lines after CO₂ exposure is shown in Figure 6. When
 228 the Cu 2p line, after CO₂ exposure, is compared to the same line before exposure (Figure

5a), the presence of more sites corresponding to a carboxylate structure formed via coordination of a bent $\text{CO}_2^{-\delta}$ molecule to a Cu center similar in binding energy to a CuCO_3 (copper carbonate) is evident [33]. The position of the Cu (L_3VV) Auger peak now shifted to at 917.2 eV, also confirmed this chemical state. The structure of the Fe 2p line did not change much. However, in this case the chemical state of Fe^{2+} cannot be differentiated between FeO and FeCO_3 because they have the same binding energy [29].

The XPS spectra for C 1s and O 1s were also taken before and after CO_2 dosage and after TPD. XPS spectra of the C 1s band are shown in Figure 7a (after CO_2 dosage) and 7b (after TPD). Adventitious carbon which appears at a binding energy of 284.6 eV was not completely removed in order to have a reference to determine binding energies of other elements due to sample surface charging. After CO_2 dosage, an important increase of the peak located at 290 eV, attributed to an increase of carbon due to CO_2 exposure, was observed. The same C 1s peak at 290 eV is significantly decreased after TPD. XPS spectra of the O 1s band are shown in Figure 8a (after CO_2 dosage) and 8b (after TPD). The O1s fitted well with peaks attributed to the bonding within metal carbonates (CO_3^{2-}) [26]. This effect shows an important increase after the CO_2 exposure, and additionally the binding energy related to adsorbed water showed an intriguing increase in intensity after TPD. Perhaps water is absorbed in the bulk of the material.

3.5 Thermal programmed desorption (TPD)

The TPD measurements were performed for different doses using a mixture of water vapor and CO₂ gas. A TDP curve for the sample of CuFe_{1-x}Ga_xO₂ which was exposed to 1500 L of CO₂ (after XPS characterization) is shown in Figure 9. The sample was heated up to 940 K at a rate of 36 K/s.

By using a TPD curve it is possible to determine the activation energy of the desorption reaction using Arrhenius equation,

$$k = A \cdot e^{-E_a/k_B \cdot T} \quad \text{Equation (4)}$$

where k is the rate constant of the reaction on the absolute temperature T. This rate can be obtained from the pressure burst during the TPD using different calculations. We used a method of area integration for the desorption curve with a method described previously [34]. From the Arrhenius plots for CO₂ and H₂O desorption we obtained the respective activation energies. The activation energy obtained for carbon dioxide desorption was E_a=0.39 eV/atom, and for water desorption 0.36 eV/atom.

There is not much information in the literature about desorption energy for CO₂ chemisorption on oxide surfaces that allows us to compare our results with other results. Pacchioni et al. [35] have theoretically analyzed CO₂ chemisorption on MgO and CaO. They found that CO₂ would be weakly bound to MgO. But in the CaO case, a chemically bound carbonate to a surface oxygen ion can be expected. A prediction of activation energy

of about 10 kcal/mole (0.43 eV/atom) for CO₂ desorption from CaO surface was estimated. The observation by XPS of a bound carbonate on the surface of ZnO was also reported previously [36].

4. Conclusions

A thin film of CuFe_{1-x}Ga_xO₂ was made using PLD evaporation. The composition of the sample is near CuFe_{0.75}Ga_{0.25}O₂ stoichiometry. Evidence of semiconductor behavior was found from the “Tauc” analysis of the samples’ characteristic transmittance. The direct band gap measured was between 2.8-3.1 eV and the indirect band gap was between 0.9-1.3 eV. The difference between these values and those of the pure CuFeO₂ Delofossite is associated with the inclusion of Ga in a solid solution and consequently producing changes to the optical characteristics of the semiconductor material. Optical transmission and reflection measurements as well as thermal programmed desorption on a CuFe_{1-x}Ga_xO₂ film sample exposed to CO₂ confirmed the chemisorption of CO₂ onto its surface. These studies reveal that the sample surface interacted strongly with carbon dioxide and water, forming chemisorbed hydroxides and carbonates on the Cu-Fe oxide surface. We can ascertain from XPS characterization that a carboxylate structure formed via coordination of a bent CO₂^{-δ} molecule to a Cu center is present. The activation energies for desorption were obtained from Arrhenius plots constructed for each gas. The desorption energy corresponding to 0.39 eV/atom was found for carbon dioxide and 0.36 eV/atom was found for water. These values agree well with CO₂ chemisorption on other metal oxide surfaces.

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Shared Research Facilities

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Figure 1. X-ray diffraction spectra for the sample $\text{CuFe}_{1-x}\text{Ga}_x\text{O}_2$ grown at 600 C in 0.1 Torr O_2 pressure. Miller indexes in black correspond to Delafossite structure while Miller indexes in red correspond to spinel structure. Inserted figure: rocking curve of sample

Figure 2. Raman Spectra of $\text{CuFe}_{1-x}\text{Ga}_x\text{O}_2$ film grown over sapphire substrate. Inserted figure: details of Raman spectra corresponding to Delafossite oxide

Figure 3. Band Gap of $\text{CuFe}_{1-x}\text{Ga}_x\text{O}_2$ film. a) Closer inspection of the spectra revealed 3 likely linear regions, possibly pertaining to 3 separate energy gaps within the thin films. The 3 energy gaps found at 2.4eV, 2.8eV and 3.1eV have been attributed to the direct band gap; b) Indirect band gap at between 0.9 and 1.3 eV.

Figure 4 Optical data of $\text{CuFe}_{1-x}\text{Ga}_x\text{O}_2$ film exposed to CO_2 atmosphere : a) TF Transmittance versus CO_2 pressure; b) TF Reflectance versus CO_2 pressure.

Figure 5. XPS spectra of (a) Cu 2p and (b) Fe 2p lines for the $\text{CuFe}_{1-x}\text{Ga}_x\text{O}_2$ film

Figure 6. XPS spectra of (a) Cu 2p and (b) Fe 2p lines of $\text{CuFe}_{1-x}\text{Ga}_x\text{O}_2$ film after 1500 L CO_2 exposure.

Figure 7. XPS spectra of C 1s line for $\text{CuFe}_{1-x}\text{Ga}_x\text{O}_2$ film (a) after exposure to 1500L of CO_2 . and (b) after TPD.

Figure 8. XPS spectra of O 1s line for $\text{CuFe}_{1-x}\text{Ga}_x\text{O}_2$ film (a) after exposure to 1500L of CO_2 . and (b) after TPD.

Figure 9. TPD curves of CO_2 and H_2O desorption from $\text{CuFe}_{1-x}\text{Ga}_x\text{O}_2$ film after 1500 L CO_2 dose.

Figure 1.

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