AIP Conference Proceedings

X-ray photoelectron spectroscopy study of chromium and magnesium doped copper ferrite thin film

Cite as: AIP Conference Proceedings **2279**, 140002 (2020); https://doi.org/10.1063/5.0023933
Published Online: 26 October 2020

Thiha Soe, Arthit Jityen, Teerakorn Kongkaew, et al.

X-ray Photoelectron Spectroscopy Study of Chromium and Magnesium Doped Copper Ferrite Thin Film

Thiha Soe[1, a)], Arthit Jityen[1], Teerakorn Kongkaew[1], Kittitat Subannajui[1], Asawin Sinsarp[2], and Tanakorn Osotchan[1,2]

[1]School of Material Science and Innovation, Faculty of Science, Mahidol University, Rama VI Road, Bangkok, Thailand.
[2]Department of Physics, Faculty of Science, Mahidol University, Rama VI Road, Bangkok, Thailand

[a)]Corresponding author: thihasoe1263@gmail.com

Abstract. X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements. Moreover, XPS is also widely used in semiconductor applications as the main characterization technique. In this work, chromium and magnesium doped copper ferrite thin films were prepared on the glass substrates by spin-coating technique at room temperature. The stoichiometry 1:2 ratio was used for copper (II) acetate monohydrate and iron (III) nitrate nonahydrate with different doping percentages from 5%, 10%, 15% to 20% of chromium and magnesium. After spin-coated, the films were annealed at 120°C, 200°C, 300°C and 400°C in air. The surface properties of the post-annealed thin films can be characterized by XPS technique due to their surface sensitivities. Therefore, the surface properties of different doped amounts of chromium and magnesium thin films were systematically investigated for different annealing temperatures. For varying anneal temperatures, the oxidation numbers of copper and iron ions were different. At low temperature, the oxidation number of copper was Cu^{+} and iron was a mixture of Fe^{2+} and Fe^{3+} while at high-temperature, the copper and iron ions showed Cu^{2+} and iron Fe^{3+} characteristics, respectively. After etching, the oxidation number of copper and iron ions at the surface shifted to lower oxidation state.

INTRODUCTION

For surface analysis, one of the key questions is the chemical state of active metal ions on the surface. The XPS is typically used in these studies because it is surface sensitive and non-destructive. Copper ferrite is one of the group members of ferrite semiconductors. A copper ferrite can be formulated as (Cu^{2+}) $[Fe2\ ^{3+}]$ O_4 where Cu^{2+} and Fe^{3+} occupy at tetrahedral (A) and octahedral (B) positions, respectively in the FCC lattice formed by O^{2-} ions. It can be used in many applications such as high-density information storage devices, targeted drug delivery, high-frequency electronic devices, MRI, gas sensors, and magnetic refrigeration systems. Doping of magnesium in copper ferrite can enhance its magnetic property[1,2]. In addition, chromium doped of copper ferrite also showed high CO selectivity in gas sensor application[3]. Many research groups focused on studying crystal structure[4-7] however the chemical state analysis of $CuFe_2O_4$ is very limited. In this present work, chemical state study of chromium or magnesium doped $CuFe_2O_4$ thin film for different annealed temperatures is systematically analysis by XPS technique.

EXPERIMENTAL SECTION

The chromium or magnesium doped copper ferrite thin films were fabricated by spin coating technique. Copper (II) acetate monohydrate ($Cu(CO_2CH_3)_2.H_2O$), iron (III) nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$), chromium(III) nitrate nanohydrate ($Cr(NO_3)_3.9H_2O$), magnesium (II) nitrate hexahydrate ($Mg(NO_3)_2.6H_2O$) and triethanolamine ($C_6H_{15}NO_3$) were used without further purification. In the first step, the precursor solutions were prepared by adding

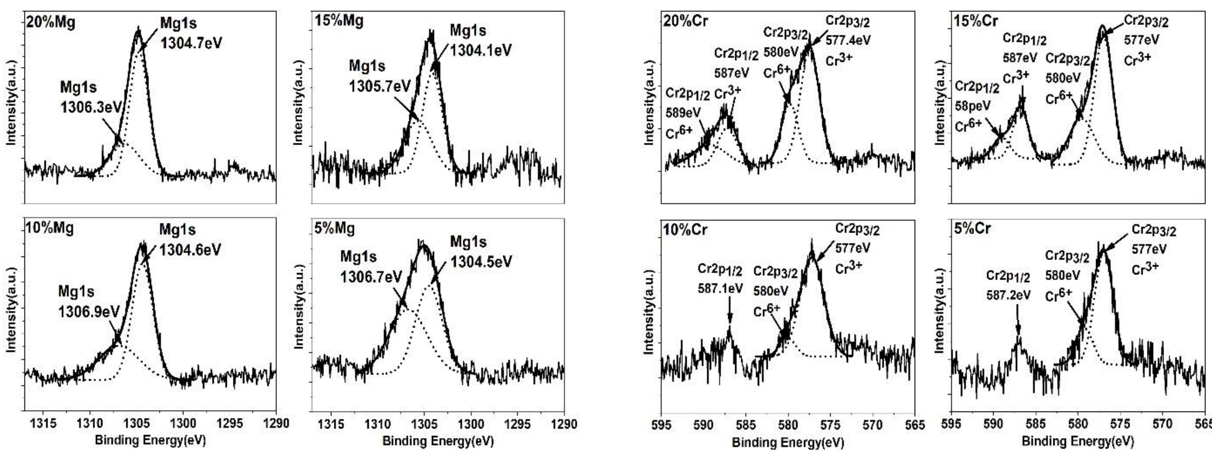
The Second Materials Research Society of Thailand International Conference
AIP Conf. Proc. 2279, 140002-1–140002-4; https://doi.org/10.1063/5.0023933
Published by AIP Publishing. 978-0-7354-4009-8/$30.00

the powder into ethanol with stoichiometric quantities and stirring for two hours. Then triethanolamine was added into the precursor solution and stirred for another twelve hours to get the homogeneous solution. The solution was then ready to be spin-coated on the glass substrate. The annealing process was done at different temperatures of 120°C, 200°C, 300°C and 400°C for one hour. The doping amounts for both chromium and magnesium doped were 5%, 10%, 15% and 20%.

XPS analyses were performed using AMICUS / ESCA 3400 **(**Kratos Analytical Wharfside) with incident monochromated X-ray beam from Al and Mg targets at 20 kV and 10 mA focused on the sample surface. The electron energy analyzer was operated with a pass energy of 75 eV enabling high resolution of the spectra to be obtained. The energy of the X-ray source for Al and Mg targets are 1486.6eV and 1253.6eV, respectively. The step size of 0.1 eV was employed and each peak was scanned for five times. The XPS binding energy was calibrated from the peak of noble metal for example silver and each XPS spectra were modified with the carbon peak.

RESULTS AND DISCUSSION

By using Al target, the Mg-doped copper ferrite thin film showed one big peak of Mg 1s spectra around 1305eV for all doping percentages which binding energy is very close to the binding energy of Mg^{2+} as reported by P Stefanov.[8] For detail analysis, the Mg1s peak can be fitted with two Gaussian peaks around 1306eV and 1305eV representing Mg^{2+} ions occupied in octahedral sites and tetrahedral sites, respectively[9]. The higher binding energy peak becomes more dominant for lower percentage Mg doping e.g. 5%. These peaks are stable for all different temperatures as shown in Fig. 1(a).



(a) (b)

FIGURE 1. XPS spectra of (a) Mg 1s peak and (b) Cr 2p peak for copper ferrite thin film doped with Mg and Cr, respectively, at concentrations of 5, 10, 15 and 20 percentages after annealing at 400°C.

For all chromium doping percentages, the chromium spectra show two main peaks around 577eV and 587eV which indicated Cr ion characteristic.[10] However, for the lower doping percentage such as 5% and 10% the peaks at higher binding energy are not significant like higher doping amount. See in Fig. 1(b). There is no shift in peaks position for different annealing temperatures. Mg target was used to analysis chromium doped.

The XPS results of Cu 2p for 20% Mg-doped copper ferrite sample annealed at 120°C, shown in Fig. 2(a), exhibited the characteristic of Cu^{+} with two main peaks of Cu $2p_{3/2}$ 933.6eV and Cu $2p_{½}$ 953.7eV and one weak satellite peak. However, for 200°C sample, Cu 2p spectrum has two main peaks and two satellite peaks which means that the spectra originated from the mixture of Cu^{+} and Cu^{2+} ions. The spectra of copper from samples annealed at 300°C and 400°C indicated Cu^{2+} characteristic with the two main peaks and two strong satellite peak.[11-15] These results indicated the same characteristics for the other doping amounts of Mg. After etching, the oxidation state of Cu ions shifted to lower oxidation state. See in Fig. 3. The Cu 2p spectra of Cr doped are also similar to those of Mg-doped.

The Fe $2p_{3/2}$ and $2p_{1/2}$ XPS peaks of Mg-doped copper ferrite thin film can be used to indicate the iron oxidation state changing from the mixture of Fe^{2+} and Fe^{3+} to completely Fe^{3+} at higher temperatures. At 120°C and 200°C, the iron spectrum has two main peaks with the binding energy of 725 eV and 711.2eV which is very similar to those of Fe_3O_4.[16] However, for the sample annealed at 300°C and 400°C, the spectra of iron show two main peaks at Fe $2p_{3/2}$ 711.5eV and Fe $2p_{1/2}$ 725eV with one satellite peak which is the characteristic of Fe^{3+}.[16-19] The Fe 2p spectra in all other doping amounts of Mg and Cr resulted similarly. See in Fig. 2(b). As shown in Fig. 3, the oxidation number of Fe ions shifted to lower oxidation number after etching.

According to Fig.2 (c), the XPS results of O 1s showed one peak with a shoulder for all samples annealed at different temperatures. The binding energy for the main peak and shoulder were 530 eV and 531.5eV which represent oxygen bonding with metal (O-M) and hydroxide (O-OH), respectively.[16] The area of O-OH peak decreased relative to that of O-M peak when the temperature increases. These results were similar to those for all Mg-doped and Cr-doped.

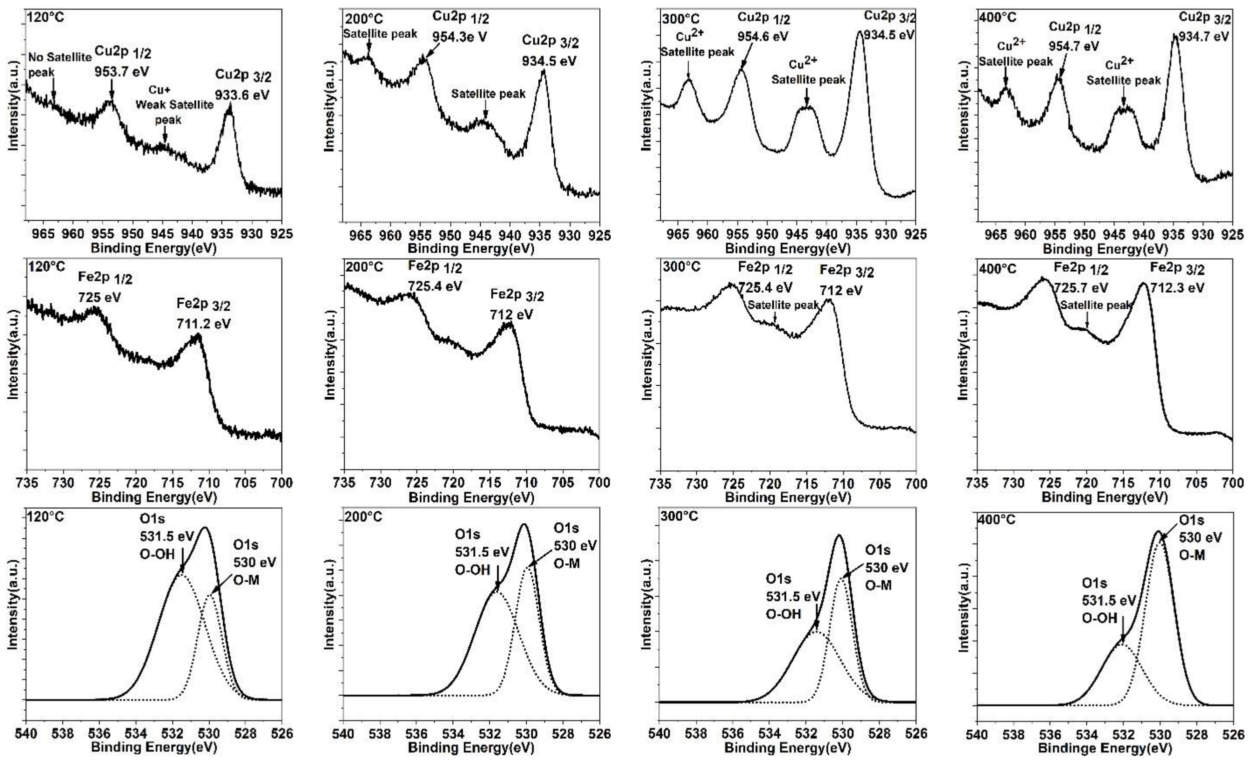


FIGURE 2. XPS spectra of Cu2p, Fe2p and O1s peaks for 20% Mg-doped copper ferrite annealed at 120, 200, 300 and 400°C

The relative atomic concentration of each element can be calculated from the XPS spectra and the derived atomic percentage proportion of Cu:Fe:O:Cr for 20% doped copper ferrite are 15.19:25.53:56.63:2.64. The atomic concentration ratio between copper and iron is about 1:1.68.

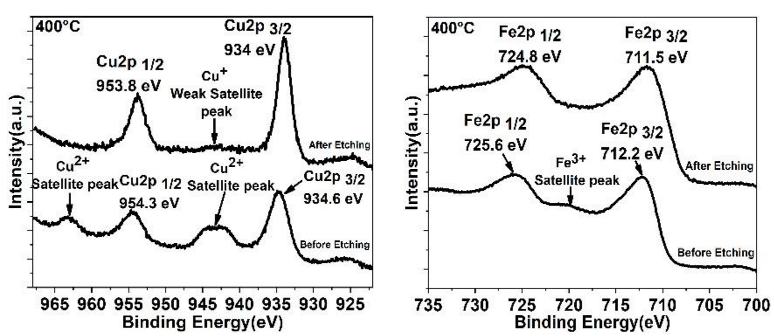


FIGURE 3. Before and after etching of XPS spectra of Cu2p and Fe2p for 20% Mg-doped copper ferrite annealed at 400°C

CONCLUSION

The Mg-doped and Cr-doped copper ferrite thin films can be prepared on glass substrates by the spin coating technique. The oxidation state of each dope element can be determined by using XPS measurements. The oxidation states of Mg 1s and Cr 2p are stable and not depend on annealing temperatures. The XPS spectra of Cu 2p and Fe 2p indicated the oxidation state of these elements and slightly modified by annealing temperature. The relative intensity of the O 1s peaks and its shoulder changes as varying the annealing temperature thus the relative intensity of O-OH peak becomes relatively lower for doped copper ferrite thin film annealed at high temperature.

ACKNOWLEDGEMENTS

The research was supported by the National Nanotechnology Center (NANOTEC) through the Research Network of NANOTEC (RNN).

REFERENCES

1. J. Huang, P. Su, W. Wu, Y. Li, X. Wu, and S. Liao, J SUPERCOND NOV MAGN **25**, 1971-1977 (2012).
2. M. A. Ahmed, H. H. Afify, I. K. El Zawawia, and A. A. Azab, J. Magn. Magn. Mater **324**, 2199-2204 (2012).
3. K. Faungnawakij, R. Kikuchi, T. Fukunaga, and K. Eguchi, Catal. Today **138,** 157-161 (2008).
4. D. Gingaşu, I. Mîndru, L. Patron, O. Carp, D. Matei, C. Neagoe and I. Balint, J. Alloys Compd. **425**, 357-361 (2006).
5. K. Zaharieva, V. Rives, M. Tsvetkov, Z. Cherkezova-Zheleva, B. Kunev, R. Trujillano, I. Mitov and M. Milanova, Mater. Chem. Phys **160**, 271-278 (2015).
6. V. Manikandan, M. Singh, B. C. Yadav and J. C. Denardin, J. Sci. Adv. Mater. Devices **3**, 145-150 (2018).
7. K. Verma, A. Kumar and D. Varshney, Curr. Appl. Phys. **13**, 467-473 (2013).
8. P. Stefanov, Vacuum **47**, 1107-1110 (1996).
9. X. Duan, X. Wang, F. Yu, and X. Liu, Mater. Chem. Phys **137**, 652-659 (2012).
10. M. Zhu, T. C. R. Rocha, T. Lunkenbein, A. Knop-Gericke, R. Schlögl and I. E. Wachs, ACS Catal. **6**, 4455-4464 (2016).
11. Y. Sakai, S. Ninomiya and K. Hiraoka, Surf. Interface Anal. **44**, 938-941 (2012).
12. V. Hayez, A. Franquet, A. Hubin and H. Terryn, Surf. Interface Anal. **36**, 876-879 (2004).
13. D. A. Svintsitskiy, A. I. Stadnichenko, D. V. Demidov, S. V. Koscheev and A. I. Boronin, Appl. Surf. Sci. **257**, 8542-8549 (2011).
14. M. C. Biesinger, L. W. M. Lau, A. R. Gerson and R. S. C. Smart, Appl. Surf. Sci. **257**, 887-898 (2010).
15. M. Fantauzzi, D. Atzei, B. Elsener, P. Lattanzi and A. Rossi, Surf. Interface Anal. **38**, 922-930 (2006).
16. T. Yamashita and P. Hayes, Appl. Surf. Sci. **254**, 2441-2449 (2008).
17. A. P. Grosvenor, B. A. Kobe, M. C. Biesinger and N. S. McIntyre, Surf. Interface Anal. **36**, 1564-1574 (2004).
18. M. Aronniemi, J. Sainio and J. Lahtinen, Surf. Sci. **578**, 108-123 (2005).
19. P. Graat and M. A. J. Somers, Surf. Interface Anal. **26**, 773-782 (1998).