

Effect of Annealing Temperature and Atmosphere to Surface Solid Phase Reaction of Sapphire Substrates and Spin-Coated Copper Nitrate Gel Films

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Abstract

The solid-phase reaction of sapphire (Al_2O_3) substrates and spin-coated copper nitrate films was studied. X-ray diffraction analysis revealed that a CuO fraction was observed by annealing at temperatures higher than 800°C . In addition, crystalline CuAlO_2 was formed at annealing temperatures in the range of 900°C - 1000°C by solid-phase reaction of the spin-coated films and sapphire substrate. Crystalline CuAlO_2 was formed by annealing at 1000°C for 5 - 10 h, and CuAl_2O_4 was formed by annealing at 1000°C for 15 h. When annealing under N_2 flow, Cu_2O was observed rather than CuAlO_2 . For a sample annealed in air at 1000°C for 5 h, X-ray photoelectron spectroscopy measurements at various depths from surface revealed that Cu^{2+} ions are located around the surface, which suggests that the CuO fraction is present near the surface while the CuAlO_2 fraction is located at greater depths from the surface of the samples. The depth profile of the sample suggests that there is no pure CuAlO_2 layer in the sample, but that crystalline CuAlO_2 is present in the sample as a mixture with CuO and Al_2O_3 .

Keywords

Solid-Phase Reaction, Sapphire Substrate, CuAlO_2 , CuO , X-Ray Diffraction, X-Ray Photoelectron Spectroscopy

1. Introduction

Cu-delafoosite, which comprises ternary metal oxide materials with a structure of CuMO_2 ($\text{M} = \text{Al, Ga, In, Sc, Y, La, Cr, Fe, etc.}$) has gathered much interest due

to their potential in various applications, such as wide gap semiconductors [1] [2] [3], catalysts [4] [5] or sensors [6]. Among the Cu-delafoosite materials, CuAlO₂ is considered a promising candidate as a p-type transparent conductive oxide (TCO) [1]. Some TCO materials, such as indium tin oxide [7] or aluminum-doped zinc oxide [8], have already been studied and applied in optoelectronic devices. However, most TCOs have n-type conductivity, so that TCO materials with p-type conductivity have been in demand to prepare transparent pn junctions. The properties of CuAlO₂ as a p-type TCO have been reported, such as an optical bandgap of 3.5 eV and conductivity of 1 Ω cm [1]. CuAlO₂ thin films have been prepared by various methods, including pulsed laser deposition [1] [9] [10], sputtering [11] [12] [13] [14], chemical vapor deposition [15] [16], solid-phase reaction of Al₂O₃, sapphire substrate, and Cu₂O thin layers [17] [18], chemical spray pyrolysis [19], and the sol-gel method [20] [21] [22] [24]. Among these preparation methods, the solid-phase reaction of sapphire substrate and Cu₂O is interesting because the CuAlO₂ layer formed on the surface of the sapphire substrate can act as a transparent electrode with strong adhesion to the sapphire substrate. On the other hand, the sol-gel method has been studied extensively as a method for the preparation of CuAlO₂ thin films. In the studies of sol-gel preparation, various aluminum source materials have been used, such as aluminum acetate [20], aluminum ethoxide [21], aluminum nitrate [22] [23], or alumatrane [24]. In addition, some of those aluminum sources do not have an exact molecular weight due to hydration water. On the other hand, the preparation of copper oxide by sol-gel method has been well established. CuO or Cu₂O thin films have been successfully prepared using the sol-gel method [25] [26]. The sol-gel films become CuO or Cu₂O thin films depending on the annealing temperature or annealing atmosphere. Films annealed under nitrogen flow at temperatures higher than 900°C generally become Cu₂O thin films, whereas CuO films are formed by annealing in air at lower temperatures [25].

In the present work, CuAlO₂ layers were prepared on the surface of sapphire substrates by solid-phase reaction of the sapphire substrate with spin-coated copper nitrate thin films. This method makes it possible to form a CuAlO₂ layer on the surface of sapphire substrate without the need for complicated vacuum equipment.

2. Experimental

A copper source solution was prepared by dissolving 2.42 g of copper(II) nitrate trihydrate in 25 mL of 2-methoxyethanol. The solution was stirred for 24 h to produce a light blue and homogenous solution. The solution was spin-coated onto a *c*-oriented single-side-polished sapphire substrate with a thickness of 0.5 mm. Before spin-coating of the copper source solution, the sapphire substrates were degreased by ultrasonication in EtOH. Spin-coating was performed at 3000 rpm for 10 s. The coated films were first heated at 200°C for 10 min in air, and then again at a higher temperature of 500°C for 20 min using a hot-plate as the

heating device. Spin-coating and subsequent heat treatment procedures were repeated 6 times to obtain a gel film with a thickness of 0.2 μm . The prepared samples were annealed at temperatures in the range of 800°C - 1100°C for 10 h in air or under nitrogen flow. In another experiment, the samples were annealed at 1000°C for 2, 5, 10 and 15 h in air. The temperature was increased from room temperature to the specific temperature over a period of 3 h, held at the specific temperature for 10 h, and then cooled to room temperature over a period of more than 3 h.

The structural properties of the films were analyzed using X-ray diffraction (XRD; D8 Discover, Bruker) in θ - 2θ mode with Cu K α radiation. A Ni filter with a thickness of 0.12 mm was used to avoid observation of the signal due to CuK β radiation. The atomic compositions of the samples, including depth profiles, were measured using X-ray photoelectron spectroscopy (XPS; JPS-9010MC, JEOL) with Mg K α radiation. Depth profiles of the samples were measured by etching with Ar sputtering. The etch rate of the sapphire substrate with Ar sputtering was determined to be 10 nm/min. The atomic compositions were determined using a sapphire substrate as a standard sample for the Al/O ratio. The Cu/Al ratios were determined using CuAlO₂ films prepared by the sol-gel method as a standard sample using Cu and Al nitrates as metal sources.

3. Results and Discussion

Figure 1 shows XRD patterns of the sapphire substrate with spin-coated copper nitrate films annealed at various temperatures (a) in air and (b) under nitrogen flow. For annealing in air at 800°C or 900°C, only peaks of CuO are observed. The CuO (110), (002)(-111) and (111) peaks are observed at 32.5°, 35.5°, and 38.7°, respectively (PDF 00-045-0937). However, the samples annealed at 1000°C showed the (006) peak of CuAlO₂ at 31.6° (PDF 00-035-1401) in addition to the peaks of CuO. At an annealing temperature of 1100°C, all the CuAlO₂ and CuO peaks disappeared, which is considered to be due to evaporation of the spin-coated copper nitrate film at high temperature before oxidation or reaction with the sapphire substrate could occur. The samples annealed under nitrogen flow showed different results. As shown in **Figure 1(b)**, a peak of Cu₂O was observed at 36.3° (PDF 00-005-0667) in addition to the peaks of CuO at annealing temperatures higher than 900°C. The intensity of the Cu₂O peak increased with the annealing temperature up to 1000°C, which is consistent with a previous study on films of CuO and Cu₂O prepared by the sol-gel route on SiO₂ substrates [25]. At an annealing temperature of 1000°C, a CuAlO₂ peak was observed at 31.7°, as was the case for the samples annealed in air; however, the intensity was very weak and the peak width was broadened.

The results indicate that the crystalline CuAlO₂ in the sample has a small volume ratio and small crystallite size. At an annealing temperature of 1100°C, no peaks were observed, similar to the samples annealed in air. **Figure 2** shows wide angle range XRD patterns of the samples annealed in air or under nitrogen flow

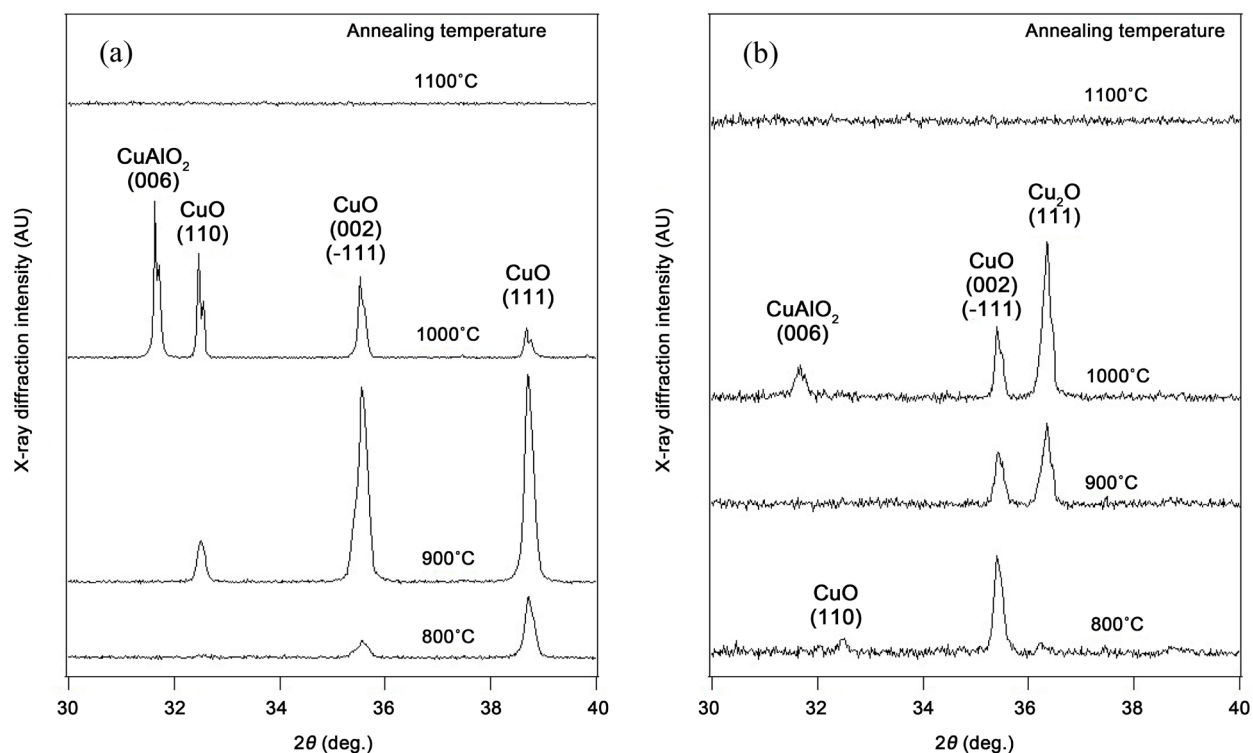


Figure 1. XRD patterns of sapphire substrates with spin-coated $\text{Cu}(\text{NO}_3)_2$ thin films annealed at various temperature for 10 h (a) in air, or (b) under nitrogen flow.

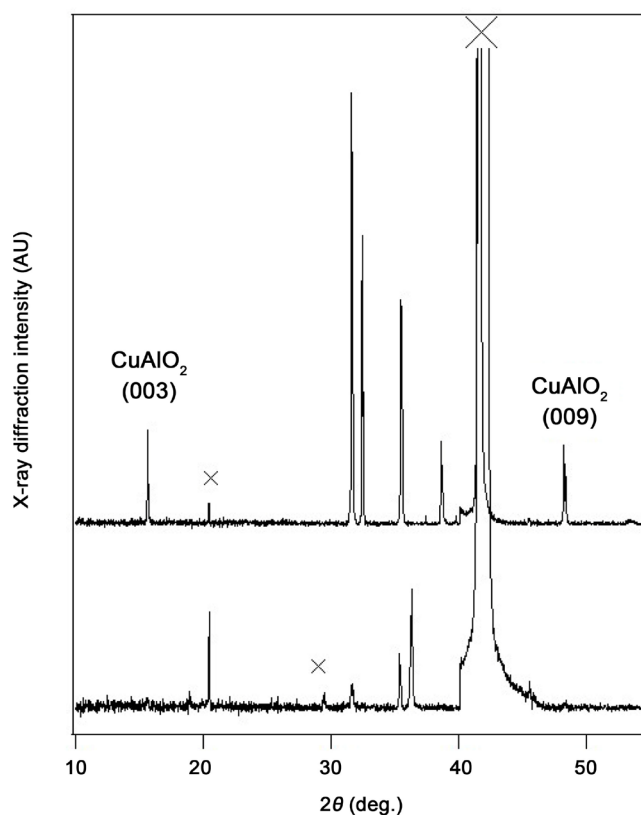
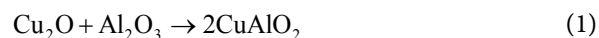


Figure 2. Wide angle range XRD patterns of samples annealed at 1000°C in air and under nitrogen flow. The peaks with cross mark are due to substrate.

at 1000°C to compare the effect of the annealing atmosphere. For the sample annealed in air, peaks of CuAlO₂ were observed at 15.6° (003), 31.6° (006), and 48.3° (009). However, no peaks beside the *c*-axis oriented CuAlO₂ peaks were observed, which indicates that the CuAlO₂ in the samples is highly *c*-axis oriented. In contrast, the sample annealed under nitrogen flow shows only one (006) peak for CuAlO₂ at 31.6°. These results indicate that annealing in air is more preferable than annealing under N₂ flow to form CuAlO₂ by solid-phase reaction between a spin-coated copper nitrate film and sapphire substrate. In the case of solid phase reaction of powders, the CuAlO₂ formation reaction under nitrogen flow is preferable than in the air.

At the temperature of 1000°C, copper oxide takes form of Cu₂O, even if the atmosphere includes oxygen gas. Thus, CuAlO₂ is formed by the solid-phase reaction shown in (1) as well as in the case of solid phase reaction of powders [14].



However, the solid phase reaction in the present work is accompanied by diffusion of oxygen and copper into sapphire substrate. In the annealing under nitrogen flow, it is considered that the supply of oxygen to the reaction interface is not sufficient and the formation of CuAlO₂ stops at a specific depth. As a result, the formation reaction of CuAlO₂ by the annealing in air becomes rather preferable than that under nitrogen flow.

In the XRD patterns of the samples annealed in air, no peaks of Cu₂O are observed, although Cu₂O is required to the solid phase reaction to form CuAlO₂. It is because the Cu₂O which exist at the temperature of 1000°C is oxidized to CuO by air at lower temperature during the temperature decreasing process in the annealing.



As a result, XRD patterns show peaks of only CuAlO₂ and CuO.

Figure 3 shows XRD patterns of samples annealed at 1000°C in air for various times. The sample annealed for 2 h showed only peaks due to CuO. In contrast, after annealing the sample for 5 h, XRD peaks of CuAlO₂ were observed with peaks of CuO. After annealing of 10 h, both CuAlO₂ and CuO peaks were observed, as with the sample annealed for 5 h. The intensity of both the CuAlO₂ peaks increased with annealing time from 5 h to 10 h. In the sample annealed at 1000°C for 15 h, a different XRD pattern from the sample annealed for 10 h was observed. The sample does not show either CuO or CuAlO₂ peaks, but instead peaks of CuAl₂O₄ are observed at 31.3° (220) and 36.9° (311) (PDF 00-033-0448). These results suggest that CuAlO₂ reacts with the sapphire substrate:



No specific annealing time was determined when the sample produced only the CuAlO₂ crystalline phase. The sample annealed for more than 20 h showed no copper related XRD peaks. This is considered to be due to the further diffusion

of Cu atoms into the sapphire substrate. This suggests that the samples annealed for more than 20 h become copper-doped sapphire substrates, whereby only XRD peaks of crystalline Al_2O_3 are observed.

Figure 4 shows an XPS spectrum for the surface of the sample annealed at 1000°C for 5 h. Peaks of Cu 2p, O 1s, and Al 2p are observed at binding energies of and 930 - 955 eV, 531.2 eV, and 74.4 eV, respectively. Peaks at binding energies of 745, 766, and 780 eV are ascribed to Auger electrons (O KLL). Cu 2p has

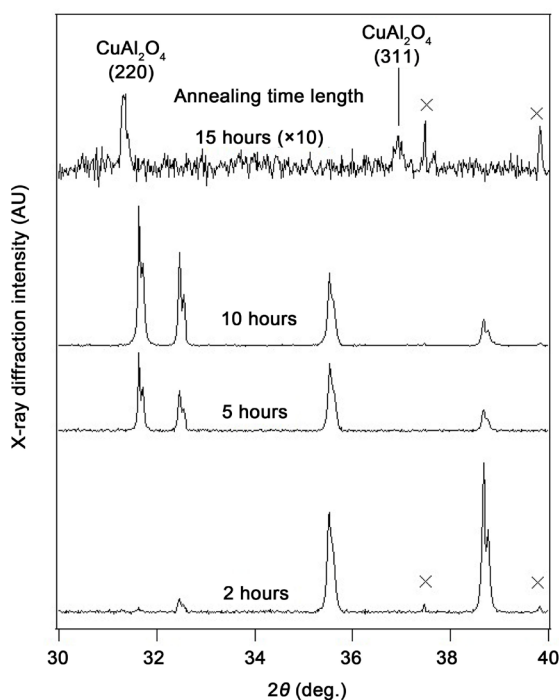


Figure 3. XRD patterns of sapphire substrates with spin-coated $\text{Cu}(\text{NO}_3)_2$ thin films heat treated for various times at 1000°C in air.

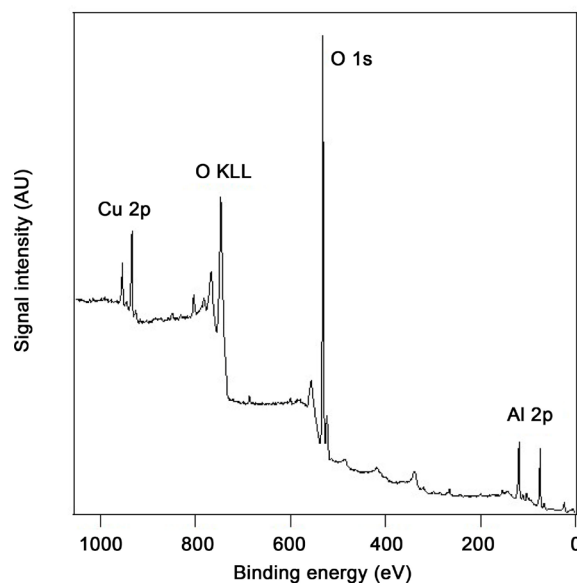


Figure 4. XPS spectrum for the surface of the sample annealed at 1000°C for 5 h.

two peaks at 933.4 eV and 953.2 eV, which are assigned to Cu 2p_{3/2} and Cu 2p_{1/2}, respectively. The peak positions observed in **Figure 4** are shifted from those for CuAlO₂ or CuO reported previously [27] [28] because the sample in the present work contains not only CuAlO₂ and CuO, but also Cu-doped Al₂O₃.

Figure 5 shows depth profile of the atomic concentrations for the sample annealed at 1000°C for 5 h. The atomic concentration of copper is 25% at the surface, which then decreases monotonically with increasing depth from the surface and becomes 0% at a depth of 450 nm. XRD measurements showed the sample contains not only crystalline CuAlO₂ but also crystalline CuO; therefore, the sample is considered to consist of both of CuAlO₂ and CuO fractions or layers embedded in the Al₂O₃ substrate. The XRD patterns of the sample measured after etching of the surface to 500 nm showed no copper related peaks.

Figure 6 shows XPS of Cu 2p, O 1s, and Al 2p spectra at various depths from

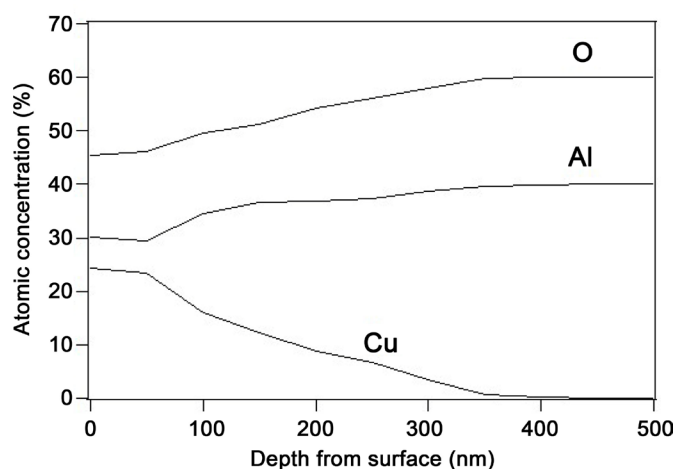


Figure 5. Depth profile of atomic concentration for the sample annealed at 1000°C for 5 h.

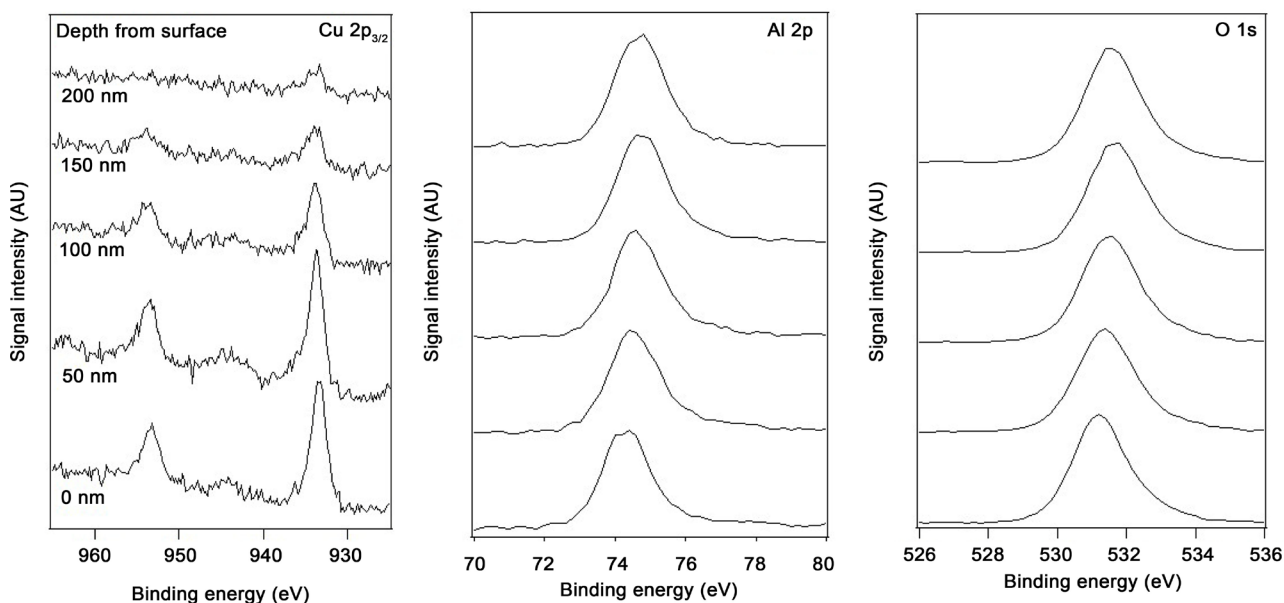


Figure 6. XPS of Cu 2p, Al 2p, and O 1s spectra measured at various depths from the surface.

the surface. XPS peaks of Cu 2p, *i.e.*, Cu 2p_{3/2} at a binding energy of 933.5 eV and Cu 2p_{1/2} peaks at 953.2 eV, are observed with a decrease in peak intensity with an increase in the depth from the surface. In addition, a weak and broad signal is also observed at a binding energy of 944 eV, which is assigned as a satellite peak that has been reported as a shake-up signal of Cu²⁺ [27]. It has been reported that the shake-up signal has not been observed in the case of Cu⁺, because of multiplet splitting of the signal [29]. The relative intensity of the signal at the surface is significantly weaker than that for pure CuO reported previously [30], which suggests that both Cu²⁺ and Cu⁺ are present at the surface, so that both CuO and CuAlO₂ are present at the surface. The relative intensity of the satellite peak to the peak at 933 eV is dependent on the depth from the surface. The shake-up signal is clearly observed in the spectra measured at the surface and at a depth of 50 nm. However, the satellite peak is not observed clearly at depths greater than 150 nm, which indicates that Cu²⁺ is present mainly around the surface. Therefore, CuO is present at surface, while CuAlO₂ is present at greater depths from the surface. In the case of the XPS O 1s and Al 2p peaks shown in **Figure 6**, the dependence of the binding energy on the depth from surface was observed as a peak shift. At the surface, the O 1s peak is observed at a binding energy of 531.2 eV, which is then shifted to 531.5 eV at a depth of 200 nm from the surface. The XPS Al 2p peak at surface is observed at 74.4 eV, which is then shifted to 74.7 eV at a depth of 200 nm from the surface. However, the peak shift is not significant, with the shift of binding energy at only 0.3 eV for both the O 1s and Al 2p peaks.

4. Conclusion

The solid-phase reaction of sapphire substrate and spin-coated copper nitrate thin films by thermal annealing was studied. XRD analysis revealed that both CuO and CuAlO₂ fractions were formed at an annealing temperature of 1000°C for annealing times of 5 h or 10 h. The formation of CuO is due to oxidation of the spin-coated copper nitrate gel film by the sol-gel route reaction. In contrast, the formation of CuAlO₂ is evidence for the occurrence of a solid-phase reaction. XPS measurements revealed that CuO is present around the surface, while the CuAlO₂ fraction is located at greater depths from the surface.

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