Effects of solution concentration on the structural and optical properties of CuAlO2 thin films prepared on 4H-SiC via sol-gel method

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Abstract. In this work, the effects of solution concentration on the crystal structure, optical properties and surface morphology of the CuAlO2 thin films prepared on 4H-SiC (0001) by sol-gel method were studied. X-ray diffraction (XRD) indicates that the CuAlO2 films are polycrystalline and have a high preferential growth orientation (012). In addition, four emission peaks were observed from room temperature photoluminescence (PL) spectra. The emission peaks at 360 nm (3.45 eV) and 380 nm (3.26eV) are near band edge emission of CuAlO2 film and 4H-SiC substrate, respectively. The other two emission peaks at 410 nm (3.02 eV) and 470 nm (2.64 eV) arises from Cu-vacancy defect. The surface roughness of the films was increased in the case of high solution concentrations, resulting a reduction in the optical transmittance. However, an overall improvement in crystallinity of the films and reduction of Cu-vacancy defect was observed with the increased solution concentrations.

1. Introduction
Silicon carbide (SiC) has been proved to be a very promising semiconductor material suitable for high-power, high-temperature and high-radiation applications owing to excellent physical properties such as wide bandgap, high thermal conductivity and high breakdown electric field strength [1,2]. SiC bipolar devices are potentially very suited for ultrahigh-voltage (>10kV) power devices because the resistance of the thick voltage-blocking layer can be reduced via modulation of the conductivity [3]. However, due to the relatively high ionization-energy (0.19eV) of aluminum (Al), which can serve as a main p-type dopant in SiC, the p'-n emitter junctions in SiC bipolar devices show a poor injection capacity at room temperature [4], which increases both forward voltage drop and switch-on time of the devices.

The delafossite-structure CuAlO2 has a large wide direct bandgap(>3.5eV) and high transparency at room temperature. In addition, CuAlO2 exhibits a high intrinsic p-type conduction which is essential for electronic applications. Ever since CuAlO2 was first realized by Kawazoe and co-authors in 1997 [5], the advantages of CuAlO2 have gained significant attention for its applications in solar cells [6],
light-emitting diodes [7,8], and chemical sensing devices [9,10]. Compared with p-SiC, the even wider bandgap CuAlO₂ makes it feasible to use CuAlO₂ as the p⁺ emitter to overcome the poor injection capacity of p⁺-n emitter junctions in SiC bipolar devices. However, to the best of our knowledge, there have been no reports on the CuAlO₂/SiC heterojunction. Meanwhile, the preparation of high quality CuAlO₂ films on SiC substrates is essential to achieve CuAlO₂/SiC heterojunction with better device performance. Among various production methods employed to fabricate CuAlO₂ films, sol-gel method has advantages such as easier composition control and less expensive. In addition, the solution concentration is a significant process parameter as for the preparation of CuAlO₂ films on SiC substrates via sol-gel method [11].

In this paper, we demonstrate the preparation of CuAlO₂ thin films on 4H-SiC using the sol-gel method. The dependences of the structural and optical properties of the CuAlO₂ thin films on the solution concentration are analyzed and discussed.

2. Experiment
The CuAlO₂ thin films were prepared on SiC substrates using the sol-gel method. Anhydrous copper acetate (Cu(C₂H₃O)₂) and nonahydrate aluminum nitrate (Al(NO₃)₃ꞏ9H₂O) were used as precursors with a mole ratio of 1:1 to synthesize CuAlO₂ coating solutions, which were dissolved into dimethylformamide and stirred for 30 minutes to form mixed solutions. Ethanolamine was added to the solutions to obtain homogeneous solutions. Solutions with concentrations of 0.1 M, 0.3 M, 0.5 M and 0.7 M were obtained by varying the amount of precursor. The solution was then stirred for 5h to yield a clear and bluish homogeneous solution, which served as coating solution after 12 h of rest at ambient temperature. Prior to deposition, 10×10 mm² n-type (0.1Ω·cm) 4H-SiC substrates, which were cut from a (0001) 4H-SiC wafer 4°off-axis towards the [11-20] direction produced by TankeBlue Semiconductor Co. Ltd, were cleaned using a standard cleaning process [12]. Droplets of the solution were spin-coated onto the Si-face of the 4H-SiC substrates at a speed of 3000 rpm for 30 s. The deposited films were preheated on a hot plate at 250 °C for 20 min. Spin-coating and preheating were repeated three times. All deposited films were annealed in a quartz tube furnace at 900 °C for 2 h under an N₂ atmosphere with a temperature-ramp rate of 5 °C/min. After annealing, the furnace was naturally cooled down to room temperature.

The surface and cross-sectional morphologies of the CuAlO₂ films were measured using a JEOL JSM-6700F field-emission scanning electron microscope (FESEM). The crystal structure of CuAlO₂ films was studied using Bruker D8 discover X-ray diffractometer (XRD) with a Cu-Kα radiation (λ=0.154 nm). The UV-visible absorption spectra were recorded using a Perkin Elmer Lambda 950 UV-Vis spectrophotometer. Furthermore, the room temperature photoluminescence (PL) measurements were performed on a FLS980 fluorescence spectrometer (Edinburgh Instruments) using with an excitation wavelength of 325 nm.

3. Results and discussion
3.1. Crystal structure
Fig. 1(a) shows an 0-2θ XRD patterns of the CuAlO₂ films prepared using the solutions with concentrations in the range of 0.1 M-0.7 M. For all prepared films, the diffraction peaks at 35.85°, 37.83°, 44.36° and 64.345° correspond to SiC substrate, (012) plane of CuAlO₂, (400) plane of CuAl₂O₄ and (110) plane of CuAlO₂, respectively. In addition, the diffraction peak at 21.24° was observed for films prepared with solution concentrations of 0.1 M and 0.3 M, which correspond to (10-2) plane of Al₂O₃. These suggest that the films consist of mixture of delafossite CuAlO₂ phase and impurities of spinel CuAl₂O₄ and Al₂O₃. It has been found that spinel CuAl₂O₄ originates from the reaction between Al₂O₃ and CuO [13], which are intermediates during annealing process in the sol-gel method [14]. Meanwhile, the CuAlO₂ preferentially grows on the (11-20) and CuAl₂O₄ grows on the (0001) plane [15]. In this study, as the substrates were cut from a 4H-SiC (0001) wafer with 4°off-axis towards the [11-20] direction, the growth surfaces correspond to both the (0001) and (11-20) planes
and favor the formation of both CuAlO$_2$ and CuAl$_2$O$_4$. However, it is noteworthy that the delafossite CuAlO$_2$ phase is the predominant phase based on the sharp and intense diffraction peak. The XRD patterns also indicate that the polycrystalline CuAlO$_2$ films has a high preferential growth orientation (012). Likewise, the intensities of CuAlO$_2$ (012) enhance with the increase of solution concentrations, as shown in Fig. 1(b), indicating the improvement in crystal quality of the thin films. The average grain sizes are estimated from the full width at half maximum (FWHM) of CuAlO$_2$ (012) using the Debye-Scherrer (DS) equation [16], given by

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

Where $D$, $\lambda$, $\beta$ and $\theta$ are grain size, the wavelength, the full width at half maximum and Bragg’s angle, respectively. As shown in Table 1, there has been a slight enlargement in the grain sizes with the increase of solution concentrations.

![Fig.1 (a) XRD patterns of the CuAlO$_2$ films prepared on 4H-SiC (0001) substrate with different solution concentrations. (b) Magnified XRD patterns of the (012) peaks of the CuAlO$_2$ films](image)

| Solution concentration (M) | 0.1  | 0.3  | 0.5  | 0.7  |
|-----------------------------|------|------|------|------|
| grain size (nm)             | 31.42| 32.96| 34.04| 34.78|

3.2. Surface morphology
Fig. 2 shows the SEM and cross-section morphologies of the prepared CuAlO$_2$ thin films. The surfaces of the CuAlO$_2$ thin films prepared with solution concentrations of 0.1 M and 0.3 M are relatively smooth with no pores and cracks and the grains on the surface are observed occasionally. When the solution concentration is increased to 0.5M and 0.7M, more bigger grains with dimensions exceeding 100nm are dispersed on the surface, causing an inhomogeneous morphology. This may be due to the increased viscosity of the sol at high solution concentration and insufficient evaporation of organic compounds during the heat treatment. The interfaces between the CuAlO$_2$ films and the 4H-SiC substrates are clearly visible, as shown in the cross-sectional morphology in the insets of Fig. 2. The interior of the films consists of relatively small and homogeneous grains of about 30nm in diameter. In addition, the thicknesses of the CuAlO$_2$ thin films prepared on 4H-SiC increase with the solution concentrations increases, which is probably due to the increased viscosity of the sol at high solution concentration [11].
3.3. Optical properties

Fig. 3 (a) shows the UV-visible transmission spectra of the CuAlO$_2$ films, which were deposited on (0001) sapphire using the same growth parameters as for the 4H-SiC substrates. The data are plotted after subtracting the contribution of the substrate. It can be seen that all the films are highly transparent, with an optical transmission exceeding 70% across the entire visible range. In addition, the transmission decreases with the increase of solution concentration. In consideration of the surface morphology of the films, the decrease in the optical transparency could be due to the increased surface scattering (Fig. 2). The fundamental absorption edge for the films were located in the ultraviolet region (<380 nm), irrespective of crystallinity and phase compositions, which is considered to be due to the band-edge absorption of the film and indicates that the films absorb ultraviolet light well. From the transmission spectrum, we could determine the optical bandgaps by Tauc’s relation [17]:

\[(\alpha h\nu)^2 = A (h\nu - E_g)\]  

where $\alpha$ is the film absorption coefficient, $h\nu$ is the incident photon energy, $A$ is a constant. The optical bandgaps were estimated by extrapolating the linear portion of the $(\alpha h\nu)^2$ versus incident photon energy ($h\nu$) as shown in Fig. 3 (b). Using the derivation, the optical bandgaps of the CuAlO$_2$ films were estimated to be 3.49 eV, 3.60 eV, 3.79 eV and 3.74 eV, respectively, which are consistent with the values published in the literature [18]. The increase of optical bandgaps reflects improvements in the crystallinity of the CuAlO$_2$ films with increased solution concentrations, which is consistent with the XRD results.
Room temperature PL characterization has been performed to study the emission properties of the CuAlO$_2$ film prepared on 4H-SiC, as shown in Fig. 4. Four distinct PL emission peaks around 360 nm, 380 nm, 410 nm and 470 nm were observed in PL spectra. The peak around 360 nm corresponds to the photon energy of 3.45 eV, which is close to the direct optical bandgaps estimated from transmission and could be ascribed as the near-band-edge (NBE) emission of the CuAlO$_2$ film [19,20]. In addition, as a large penetration depth for PL excitation laser used in this study, part of the photoluminescence intensities obtained are contributed by the 4H-SiC substrates. Therefore, the emission peak around 380 nm (3.26 eV) arises from the NBE emission of the 4H-SiC substrate. The other two peaks around 410 nm and 470 nm are attributed to the defect emission, of which the defect levels are estimated to be ~0.48 eV and ~0.87, respectively. Previous studies have reported that both of the PL peaks at 410 nm (3.02 eV) and 470 nm (2.64 eV) are ascribed to the defect emission of the CuAlO$_2$ film, Cu-vacancy (V$_{Cu}$) specifically [20,21], which is the possible origination of the p-type conductivity of CuAlO$_2$ film [22], since the formation energy of V$_{Cu}$ is the lowest among the likely acceptor defects in CuAlO$_2$. It is noteworthy that the intensity of the emission peak of the defect is weaker than that of the NBE, demonstrating that the CuAlO$_2$ film prepared on 4H-SiC is of relatively high quality. Likewise, the increase of the intensities of peaks around 470 nm with the increase of solution concentrations also indicates the improvements in the crystallinity of the CuAlO$_2$ films.
4. Conclusions
In summary, CuAlO$_2$ thin films were prepared on 4H-SiC (0001) by sol-gel method with varied solution concentration for the first time. The effects of solution concentration on the crystal structure, surface morphology and optical properties of the thin films were studied. Even though the thin films were polycrystal with impurity phases, the initial results demonstrated that an improvement in crystalline properties with the increased solution concentration. However, because the viscosity of the sol is increased at high solution concentration and the evaporation of organic compounds during the heat treatment is insufficient, degradation of surface morphology in the thin films prepared with high solution concentration was observed. Further work is required to overcome the experimental challenges to achieve high quality CuAlO$_2$ thin films prepared on 4H-SiC.

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