Tuning the Electronic and Magnetic Properties of CuAlO₂ Nanocrystals Using Magnetic Dopants

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ABSTRACT: Optoelectronic applications with transparent conducting oxides have been made possible by modulating the carrier density of wide band gap oxides with doping. We demonstrate the modulation of the density of states (DOS) at the Fermi level in nanocrystalline CuAlO₂ particles synthesized using a sol–gel technique, as a function of doping with a magnetic impurity (Ni). This behavior is directly correlated with structural studies using X-ray diffraction and magnetic properties which show a similar trend. Our results can be understood in a picture where charge hopping occurs through surface or defect states, rather than by direct hopping between the quantum-confined states of the nanocrystal, and an increase in the DOS at the Fermi level caused by the substitution of Ni atoms at the Al site.

INTRODUCTION

Transparent conducting oxides exhibiting high electrical conductivity and transparency to visible light have found applications in window layers of solar cells, front electrodes in flat-panel displays, defrosting windows in refrigerators or airplanes, and photovoltaics. A key route for such applications has been the use of wide band gap oxides for transparency and doping to modulate the carrier concentration (n-type or p-type). The delafossite oxide CuAlO₂ is a p-type transparent semiconductor that could be considered as a candidate material for such applications. More recently, they have also found applications as hole interfacial layers for diodes,7,8 as well as in the fabrication of perovskite solar cells.9 However, as a result of the peculiarities of the crystallographic structure in the bulk form, its electrical transport can be highly anisotropic and there exists a large scatter in the literature with regards to the conduction mechanism, ranging from polaron transport to variable-range hopping (VRH). The anisotropy can be understood in a picture where charge hopping occurs through surface or defect states, rather than by direct hopping between the quantum-confined states of the nanocrystal, and an increase in the DOS at the Fermi level caused by the substitution of Ni atoms at the Al site.

RESULTS AND DISCUSSION

CuAlO₂ nanoparticles were synthesized using a sol–gel method which requires cheap precursors while offering fine control of the stoichiometric homogeneity. Al(NO₃)₃·3H₂O (2.62 g, 7 mmol) and Cu(NO₃)₂·3H₂O (1.695 g, 7 mmol) were stirred in 30 mL of methanol for 45 min at room temperature. Citric acid monohydrate (C₆H₈O₇H₂O) (5.88 g, 28 mmol) was dissolved in 30 mL of water and then added to the mixture of nitrates. Then, the whole mixture was again stirred for 1 h at room temperature to obtain a well-mixed precursor solution. The solution was further stirred at 70 °C for 24 h. After the formation of gel, it was heated at 1100 °C for 6 h in a muffle furnace. The use of citric acid plays an important role in the synthesis of CuAlO₂ nanoparticles. It acts as a fuel for the combustion reaction and prevents the precipitation of hydroxylated compounds by reacting with metal precursors to form complexes. It also acts as a growth inhibitor and is responsible for the smaller size of CuAlO₂ nanoparticles. Some impurities such as CuO and CuAl₂O₄ are also formed along with the nanoparticles. To remove the impurities, purification was carried out.

In this article, we introduce a Ni dopant into nanocrystalline CuAlO₂, and investigate the modulation of the electrical and magnetic properties with doping. Structural studies using X-ray diffraction (XRD) show a shift in the CuAlO₂ peaks toward lower angles with an increase in the dopant concentration. Two-terminal transport measurements suggest that the conduction mechanism is given by VRH for all doping concentrations within the temperature range of investigation (90–300 K). Variations in the density of states (DOS) at the Fermi level, extracted from transport measurements, show a peak at 1% Ni concentration. Magnetic data show the improvement in the ferromagnetic (FM) properties at low doping concentrations (1%) and are supported by first-principles density functional theory (DFT) simulations. All the above observations are consistent with the preferential substitution of the dopant impurity, Ni, at the Al cation site for low doping concentrations.

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was carried out using 35% HCl, followed by centrifugation for 3 min at 4300 rpm and an isopropanol wash. This process was repeated twice, and the obtained powder was dried at 60 °C in an oven for 20 h.

Figure 1 shows the diffraction pattern of the prepared solids. The structure has been indexed to the rhombohedral crystal structure with a space group $R3m$. Mostly, this matches with the JCPDS pattern #09-0185. Two peaks that cannot be accounted for and are marked by stars in the figure are due to the presence of a small amount of CuAl$_2$O$_4$ (JCPDS #78-0556) that could not be washed away completely. In the rhombohedral structure, the Cu atom is linearly coordinated between the two oxygen atoms, forming a dumbbell-like structure. The Al–O coordination results in an Al-centered edge-shared octahedral structure which separates the CuO$_2$ dumbbell structure. In the delafossite structure, there are two cation sites, Cu$^+$ at position 3(a) (0,0,0) and Al$^{3+}$ at position 3(b) (0,0,1/2), and one anion site, O at position 6(c) (0,0,u). The peaks show strong intensities, suggesting a high degree of crystallinity.

Upon doping with Ni$^{2+}$ ions, a shift of diffraction peaks toward lower diffraction angle was observed, as shown in Figure 1b. Upon introduction of Ni, we observe the presence of CuO phase, as shown in Figure 1c. It could therefore be concluded that Ni$^{2+}$ ion is replacing the Cu$^+$ ion which is being pushed out of the lattice in the form of CuO. The ionic radius of Cu$^+$ (0.46 Å) is smaller than the ionic radius of Ni$^{2+}$ (0.69 Å). The larger Ni$^{2+}$ ion would then be expected to push the Cu$^+$ in an O–Cu–O dumbbell shape, resulting in the expansion of the lattice parameter and shift of diffraction peaks toward lower angles, as we have observed here. The same effect would be observed if Ni$^{2+}$ replaces an Al$^{3+}$ cation that has a 0.53 Å diameter. This substitution should also be reflected in the electronic properties of the doped materials as we show below.

The dopant percentages mentioned were measured presynthesis. We have further used energy-dispersive X-ray analysis to ensure the presence of Ni dopant. We find that the dopant percentages postsynthesis are in good agreement with the amount of Ni dopant used in the synthesis. We find the atomic concentrations of 1.8, 2.8, and 4.3% corresponding to the nominal concentrations of 1, 3, and 5%, respectively. No traces of Ni are observed in the undoped samples. The average size of CuAlO$_2$ nanoparticles was found to be 25–28 nm from XRD measurements and further confirmed by transmission electron microscopy (TEM), as shown in Figure 1d.

Transport measurements were performed on pellets made from respective powders, inside a CTI-Cryogenics closed cycle cryostat using a Keithley 2611 sourcemeter and a Keithley 6485 picoammeter. Electrical contacts to the pellets were made in a sandwich geometry using a silver paint. The samples were stored in vacuum and exposed to air to make electrical contacts. Figure 2 shows the current ($I$)–voltage ($V$) characteristics for the undoped and 1 and 3% Ni-doped samples. The $I$–$V$ characteristics are linear at low bias voltages for all temperatures measured, indicative of ohmic contact at the interface. For comparable thickness of the pellets, the current drops by orders of magnitude as the doping concentration is increased from 0 to 3%. Figure 2a–c shows the current at low bias as a function of inverse temperature for undoped (filled circles), 1% (filled squares), and 3% Ni (filled triangles) doped samples. As the samples show Ohmic behavior near zero bias, the current can be directly related to the conductivity. For all three samples, we find that the device conductivity reduces rapidly with an initial decrease of temperature but becomes weaker as we move to lower temperatures.

We investigate the temperature dependence of the current by analyzing the temperature dependence of the reduced activation energy, $w = T^x \partial \rho / \partial T^x$, following the approach developed by Zabrodskii and Zinov’eva. If the resistivity follows a power law behavior, $\rho(T) \propto \exp(T_0/T)^x$, the power law exponent can be calculated by exploring in place of $\rho(T)$, the quantity $w(T)$

$$w(T) = x(T_0/T)^x$$

$$\ln w = \ln(xT_0^x) - x \ln T$$

Figure 2. Device $I$–$V$ characteristics at various temperatures (a) 0% Ni, (b) 1% Ni, and (c) 3% Ni.
To determine the power law exponent, we plot the logarithm of \( \omega \) as a function of the logarithm of the temperature \( T \), as shown in Figure 3a. We find exponents of 0.24 ± 0.3 and 0.22 ± 0.2 for a voltage of 0.1 and 0.5 V across the undoped sample, respectively. These are consistent with Mott’s VRH in three dimensions, where the resistivity scales as \( 1/T^{2/3} \). Although the data shown in Figure 3b are for the undoped samples, similar exponents are observed for the doped samples as well.

A log–linear plot of the current as a function of \( 1/T^{1/4} \) for all three samples is shown in Figure 3c. As the \( 1/T^{1/4} \) dependence can fit our data for the temperature range studied here, the conduction mechanism is consistent with Mott’s VRH:

\[
G = G_0 \exp\left(-\left(T^*/T\right)^{1/4}\right)
\]

where

\[
T^* = 24/\pi a^2 g_0 k_B
\]

Here, \( a \) is the localization length, \( g_0 \) is the DOS at the Fermi level, and \( k_B \) is the Boltzmann constant. We note that the conduction mechanism does not change with doping.

The localization length for colloidal nanocrystals of diameter smaller than the Bohr radius has typically been found to be comparable to be of the order of the dot radius. However, there exists some scatter in the literature for the value of localization length, and length scales much smaller than the dot radius have been reported for ZnO nanocrystals. Localization lengths of the order of ~1 nm are typically reported for amorphous Ge-based semiconductors. For our larger nanocrystals, we estimate the localization length directly from the Wentzel–Kramers–Brillouin expression of the tunneling probability, \( a = 2\hbar/m^*E_B \), where \( m^* \) is the effective mass of the charge carrier and \( E_B \) is the barrier height. We look at two extreme cases of the barrier height. If we assume that tunneling only occurs between the nanocrystals through an insulating medium, it is reasonable to take a barrier height comparable to the electron affinity of the nanoparticle (in this case ~3 eV). For tunneling through an insulating barrier of height of ~3 eV, we obtain a localization length of 0.17 nm. We may then obtain the DOS at the Fermi level for each of the samples, assuming that the dopant concentration does not significantly alter the localization length. The chemical tendency of Cu to favor higher valence states enables heavy p-type doping in the material, resulting in holes as majority charge carriers. Further, hybridization between the Cu d and O p states improves the dispersion of the valence bands, resulting in an effective mass of 2.6\( m_0 \), where \( m_0 \) is the mass of an electron.

Figure 3d shows the variation of \( T^* \), as a function of the nominal Ni dopant concentration. With a working localization length of 0.17 nm, we estimate the DOS at the Fermi level as a function of dopant concentration, as shown on the right axis of Figure 3d. Although samples prepared in different batches show different DOS levels for the undoped samples, the general trend in the variation of the DOS with doping remains unchanged. A peak in the DOS is observed for 1% Ni doping. As CuAlO\(_2\) is expected to have holes as majority carriers, a substitution of Ni\(^{2+}\) at Al\(^{3+}\) sites would result in an increase in the density of free holes. The substitution of Ni ions at the Al site is consistent with diffraction shifts discussed earlier. The decrease in the DOS with further increase in the Ni concentration may be caused by the substitution of a larger percentage of Ni atoms at point defects or vacancies, and possibly at the Cu site as well. However, the increase in the DOS and the concentration of free holes would possibly compete with scattering from defects and impurities to determine the total resistance of the sample. This could explain the decrease in the current for sample of thicknesses as the concentration of Ni is increased from 0 to 1%.

The hopping distance, given by \( R = 0.75(3a/2\pi g_0 k_BT)^{1/4} \), is estimated to be 2.3 nm at room temperature and 3.1 nm at 100 K. This is much smaller than the nanoparticle diameter, suggesting that hopping is primarily between the surface and other defect states, rather than directly from one nanoparticle to the other. Similar results have also been reported for ZnO nanocrystals where the defect density was varied using UV illumination. If the hopping process mainly occurs between the defect states within nanocrystals, we choose a barrier height corresponding to typical defect or pinning states in CuAlO\(_2\) (0.3 eV). The hopping distance is expected to fluctuate if the localization length changes, possibly because of barrier height or Fermi level fluctuations. An upper limit to the hopping distance can be set by assuming a barrier height fluctuation of almost an order of magnitude, that is, 3 to 0.3 eV. We obtain new hopping distances of 9.7 and 7.4 nm at 100 and 300 K, respectively, which are still smaller than the nanoparticle diameter. Therefore, our previous suggestion that charge transport occurs through hopping between donor or surface states holds true for longer localization lengths as well. We can further estimate the critical temperature to observe Efros–Shklovskii VRH (ES-VRH):

\[
T_e = \frac{\epsilon a g_0}{k_B(4\pi e_0)^2}^{1/2}
\]

Using a dielectric constant of 7.7 for CuAlO\(_2\) we obtain a critical temperature of ~4 K for the undoped sample. This low value for the critical temperature is consistent with the absence of the
ES-VRH regime, characterized by the \( T^{1/2} \) regime in these samples. 

To probe the magnetic properties for Ni doping at the Al site and correlate the increase in the DOS with doping, we performed first-principles calculations based on spin-dependent DFT calculations using a standard plane-wave code Quantum ESPRESSO and within the generalized gradient approximation for the interaction energy of the electrons. We use ultrasoft pseudopotentials to represent the interaction between ions and electrons. An energy cutoff of 50 Ry on the plane-wave basis was used in representation of Kohn–Sham wave functions. Most calculations involved \( 2 \times 2 \times 2 \) supercells with 32 atoms corresponding to a doping concentration of 12.5%. The Ni dopants were introduced only at Al sites as the replacement of Cu sites with Ni has been the subject of multiple theoretical studies. Slab calculations were performed with \( 2 \times 2 \) supercells in the plane of the surface, after introducing a vacuum of 15 Å and allowing for surface reconstruction. Brillouin zone integrations were sampled with a \( 6 \times 6 \times 6 \) Monkhorst–Pack mesh. Structural optimization was carried out with Broyden–Fletcher–Goldfarb–Shanno algorithm to minimize energy using Hellmann–Feynman forces.

We study the DOS when Ni is substituted at the Al site for bulk and slab geometries of CuAlO\(_2\). The slab mimics the surface effects expected from a nanocrystalline sample. Figure 4a shows the orbital-projected DOS for undoped CuAlO\(_2\) (top panel) and with 12.5% Ni doping. The shaded areas represent the Cu d states and Ni d states in the top and bottom panel, respectively. The Fermi energy has been set to 0 eV for both cases. As the replacement of an Al atom by a Ni atom introduces a hole in the valence band, we can find that the Fermi level falls on the spin-up states with primary contributions from Ni d states. We find that the FM state is lower in energy as compared to the nonmagnetic (NM) state by 0.16 eV. For a slab geometry, we find that the lowest energy configuration is achieved when an Al atom on the surface is replaced by Ni, as opposed to an Al site in the interior. In this configuration, the FM state is lower in energy than the NM state by 1.22 eV. The FM configuration where an Al atom in the interior is replaced with a Ni atom is lower in energy by 0.08 eV.

Figure 4b shows the experimentally observed magnetic moments as a function of applied magnetic field, \( H \) at a temperature of 10 K. The inset shows hysteresis loops observed at low fields. We find that the undoped CuAlO\(_2\) also shows a finite hysteresis loop. This is consistent with the previous reports on CuAlO\(_2\), where this behavior is attributed to the existence of point defects which give rise to magnetic properties even in the absence of magnetic dopants. The samples doped with 1% Ni show the maximum moment and largest hysteresis loop area. However, the FM behavior decreases with further increase in Ni concentration. This is presumably due to oxygen-mediated anti-FM superexchange interactions between the adjacent Ni ions, which suppress the FM coupling.

**CONCLUSIONS**

In conclusion, we have investigated the modulation of structural, electrical, and magnetic properties of Ni-doped CuAlO\(_2\) nanoparticles. The transport mechanism is given by Mott’s VRH between the localized surface and defect states and is robust to doping with Ni. Structural investigations reveal a shift of diffraction peaks to lower angles with doping, suggesting the substitution of Ni atoms at Al sites rather than Cu sites. A modulation in the DOS at the Fermi level is obtained from transport measurements, with a peak in the DOS at 1% doping concentration, consistent with the replacement of Al\(^{3+}\) cation with the Ni\(^{2+}\) ion for low doping concentrations. At higher concentrations, the Ni ions possibly replace the Cu\(^+\) cations and defect sites, resulting in a decrease in the DOS at the Fermi level with further increase in the doping concentration. First-principles DFT calculations support the increase in the DOS with Ni doping, due to the contribution from Ni d states, and stabilization of FM order in the system. Magnetic measurements also support improvement in FM properties at low doping concentrations (1%) and decrease of FM behavior with further increase in doping.

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**Notes**

The authors declare no competing financial interest.

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