Structural and spectroscopic studies of Cu-doped NiO thin films

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Background

Nickel oxide (NiO) is a wide-band gap p-type oxide semiconductor with good optical transparency and high chemical stability [1, 2]. These properties have been exploited for applications in photovoltaics and light-emitting diodes as a hole-transporting layer [1, 2]. Doping NiO with other metal elements, such as Cu, is an effective way to adjust its grain size, crystallinity, transmittance, and ultimately its conductivity for wider use in optoelectronic devices [2-4]. Polycrystalline Cu-doped NiO films have been fabricated with different techniques using mainly glass substrates. However, studies on single-crystal thin films are lacking, even though they are fundamental to understanding the interplay between structure and functionality of doped NiO films. In this work, we have employed electron microscopy methods in conjunction with photon spectroscopies to gain insight into the role of Cu concentration on the structural, optical, and electronic properties of NiO films grown by Molecular Beam Epitaxy (MBE) as a function of doping/alloying concentrations.

Methods

A series of Ni1-xCuxO thin films with five different Cu nominal concentrations (x = 0, 3, 6, 10, 24, and 42 at.%) were grown on (001)-oriented MgO substrates by MBE. The structural, optical, and electronic properties of the grown films were characterised by in-situ reflection high-energy electron diffraction (RHEED), X-ray diffraction (XRD), ultraviolet-visible spectroscopy (UV-Vis), energy dispersive x-ray spectroscopy (EDX), X-ray photoemission spectra (XPS), atomic force microscopy (AFM), scanning transmission electron microscopy (STEM), electron energy loss spectroscopy (EELS), and current-voltage (I-V) and hot probe measurements.

Results

The in-situ RHEED analysis of the grown films shows the presence of diffraction spots along modulated RHEED streaks for undoped and 3 at.% Cu-doped NiO (indicative of layer-by-layer growth) and distinctive transmission spots (indicative of 3D island growth) for higher Cu concentration doping, with segregation of the Cu metallic phase as the Cu content reaches 10 at.%. XRD results and diffractogram patterns from cross-sectional HAADF-STEM images show the structure of the grown films remains a single crystal cubic with [001] as the preferred growth orientation, with polycrystallinity developing as Cu content exceeds 10 at.%, with observation of the Cu metallic phase in 42% Cu:NiO films (Figure 1a–c). An increase in Cu concentration also results in increased surface roughness, as confirmed by AFM and cross-sectional HAADF-STEM images. The STEM-EDX maps show a uniform distribution of the Cu in 3 at.% Cu-doped NiO film, Cu ions are likely to be substituted for Ni ions, and a segregation of Cu grains as Cu concentration increases (Figure 1d-f), which is further confirmation of Cu-phase segregation. The correlation between EELS and XPS indicates the existence of a mixture of oxidation states of Cu (Cu0, Cu+, and Cu2+) up to 10 at.% of Cu, with Cu0 becoming dominant as its concentration increases. The UV-vis absorption spectra show that an increase in Cu content results in a redshift of the absorption edges, leading to a decrease from 2.8×10^in the band gap of the grown films as Cu concentrations increase. The band gap measurements by EELS were correlated to UV-VIS measurements and were found to be in good agreement. The electrical measurements show the conductivity of NiO films increases -5 (Ω.cm)^-1 for un-doped NiO thin film and reaches the highest value of 4.1×10^-1 (Ω.cm)^-1 for NiO film with 42 at.% Cu.

Conclusion

Undoped NiO and low Cu-doped NiO films are grown as a single crystal film, and as Cu exceeds 10 at.%, it starts segregation and forms secondary phases within the NiO film. The Cu doping increases the surface roughness, as confirmed by RHEED, AFM, and STEM. The band gap of the grown films decreases as a function of Cu concentration. The characterization techniques indicate that at the lowest Cu concentration (3 at.%), Cu ions seem to be substituted for Ni ions, and as Cu concentrations increase, Cu likely starts segregating and forming Cu grains within the films. Cu phase segregation is very likely responsible for the conductivity transition from p-type to n-type properties of NiO film with increasing Cu concentrations. This result could open the door for new applications where Cu-doped NiO can be applied as p-type, n-type, or both layers in the same devices.

Graphic:

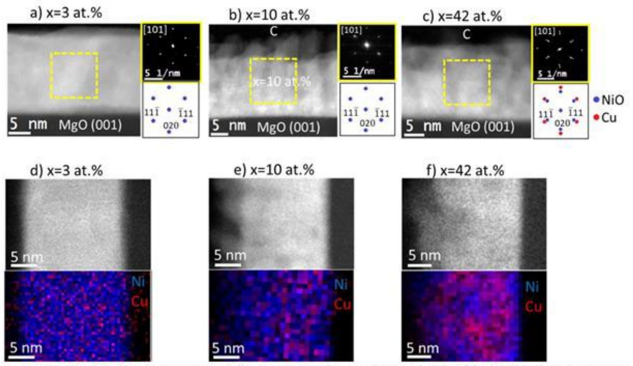

Figure 1 a-c) HAADF-STEM images of $Ni_{1-x}Cu_xO$ thin films with corresponding diffractogram patterns representing the grown film phase, and d-f) STEM-EDX maps of $Ni_{1-x}Cu_xO$ thin films, Ni and Cu in blue and red colour, respectively.

Keywords:

STEM, AFM, EELS, NiO, doping

Reference:

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