

Fabrication and Properties of Amorphous Zinc Oxynitride Thin Films

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Zn–O–N thin films fabricated by reactive radio frequency magnetron sputtering have been investigated for their compositional, structural, transport and optical properties. In contrast to processes in which the reaction for either the oxide or the nitride is dominant, the multireaction process yields a substantially amorphous films with the Hall mobility within the range from 15 to 80 cm²/(V s). In addition, it has been observed that the Hall mobility increases for Zn–O–N. Since it has a narrower bandgap than ZnO, it is put forward that the high mobility is due to the valence band maximum in this material lying above the trap states in the gap commonly observable in ZnO. These traps originate from oxygen vacancies and are localized at the bottom of the band gap influencing the carrier mobility.

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1. Introduction

Multi-cationic and multi-anionic amorphous oxide semiconductors (AOS) are the subject of intensive theoretical and experimental research aimed at applications in thin-film transistors (TFTs), as an enabling technology for novel displays, communication, computing, sensing, and identification devices [1, 2]. This material group offers a wide range of potential applications — from transparent semiconductor devices and electronic systems, to a whole range of optical and chemical sensors, manufactured on both rigid and flexible substrates. Oxide semiconductors composed of In, Ga, Sn, Ag, and Zn cations combine an X-ray amorphous microstructure and optical transparency in visible wavelength spectrum with controllable electrical conductivity from highly conductive to highly-resistive. An unique aspect of AOS is that the carrier mobility is not sensitive to the thin film microstructure, as is case of conventional covalently-bonded semiconductors. This fact arises from the nature of the chemical bonding in these metal oxides. Carrier transport in covalently-bonded materials, such as Si, is carried out primarily through anisotropic sp^3 orbitals, so that introducing randomness into the structure greatly reduces bond overlap and carrier mobility. In AOS, the higher ionicity of the bonds leads to the formation of the conduction band from the spherical s orbitals. Since the overlap of s orbitals is not significantly altered by the introduction of structure randomness, carrier transport and thus mobility is insensitive to the amorphization [3].

Amorphous In–Ga–Zn–O (a-IGZO) has attracted much attention as a channel material for TFTs owing to its electron mobility above 10 cm²/(V s) already achieved by room-temperature fabrication methods [1]. However,

a mobility considerably higher than 10 cm²/(V s) cannot be achieved in such multi-metal compounds due to potential fluctuations within the conduction band, that arise from the random distribution of the different cations. The presence of potential barriers may be explained based on the model of overlapping of s -orbitals wave functions. Even by excluding the complexity of randomness in an amorphous phase, it may not be thermodynamically favorable to pack cations of different metals in such a way that the distance between neighboring metal cations will be smaller than the distance of the interactions between s -orbitals of these cations [3, 4]. Therefore, it could be expected that there will be areas where the inter-cation distances are larger than the radii of their s -orbitals, causing interruptions in the conduction band minimum, giving rise to potential barriers, and limiting carrier mobility. Another factor suppressing carrier mobility is the presence of donor-like oxygen vacancies (V_o) located within the wide bandgap of AOS. Therefore, a promising approach to further increase carrier mobility in AOS is the formation of a single-metal compound with multiple anions suppressing such potential fluctuations [2, 5].

Several research groups already reported the possibility to control the valence band through substituting oxygen anions by non-oxide anions, such as N³⁻, S²⁻, Se²⁻, F⁻ [6–8].

Here, we present the results of the incorporation of larger size anions, namely N³⁻ with higher p orbital energy than oxygen into ZnO. At large nitrogen densities, such approach does not cause p -type doping but results in the formation of an amorphous alloy, where the anion site disorder stabilizes the amorphous phase, forming amorphous Zn–O–N thin films. This does not lower the electron mobility because the disorder is in valence band states, and not the conduction band states. Another important effect is that the N $2p$ orbital lies higher than the O $2p$ orbital, so that the new N $2p$ states raise the valence band maxima above its energy in ZnO [5, 6]. As a result,

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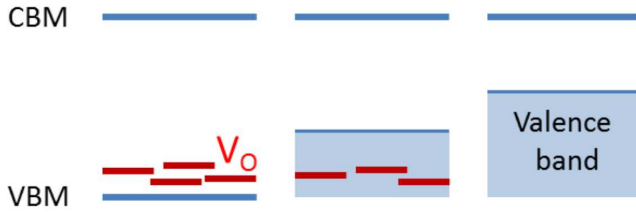


Fig. 1. Schematic band diagrams of ZnO, Zn-O-N, and Zn₃N₂, showing valence band maximum (VBM), conduction band minimum (CBM) and donor-like states within the bandgap originated from oxygen vacancies (V_o — red lines).

the initial localized trap states are now covered up by the higher valence band maximum states, so they can no longer give lower the carrier mobility [2]. A schematic of this idea is depicted in Fig. 1.

2. Experimental details

Zn-O-N thin films with a thickness of 100 nm were deposited on unheated quartz substrates, by a reactive radio frequency (rf) magnetron sputtering in Ar/N₂/O₂ plasma in a Leybold Z400 system, from 75 mm diameter metallic Zn target of 4N purity, at a pressure (P_{tot}) of 1 Pa. The oxygen to nitrogen ratio (O₂:N₂) in the sputtering atmosphere was varied between 1:20 and 1:100. The cathode current was maintained at the level of 150 mA. The composition of ZnON films was inferred from the Rutherford backscattering spectrometry (RBS) using 2 MeV He⁺. To enable precise measurements of composition, complementary Zn-O-N films were deposited on (111)-oriented Si substrate. SIMNRA program was used to simulate experimental RBS spectra. Structural analysis was performed using Philips X'Pert Pro Alpha1 Multi Purpose Diffractometer. The resistivity of thin films was determined from four-point probe measurements with a JANDEL RM3-AR apparatus. Carrier type, concentration and mobility were evaluated from the Hall measurements in the van der Pauw configuration at a magnetic field of 0.44 T, by means of a Phys Tech RH2035 setup. Ohmic contacts were fabricated by sputter deposition of Ti/Al bilayer. For optical characterization, transmittance measurements in the wavelengths range 250–950 nm, by means of a SENTECH SE800E spectroscopic ellipsometer were performed.

3. Results and discussion

By varying the N₂ and O₂ content in plasma at fixed Ar flow rate, the anion ratio in Zn-O-N was modulated, while maintaining Zn concentration at ≈55 at.%. As presented in Fig. 2a, the nitrogen content was found to increase with the O₂:N₂ ratio, constituting from below 5 to 42% of the atoms in the film, while the oxygen fraction decreased from 40% to 3%. Figure 2b shows the XRD measurement results of the Zn-O-N films. Wide-angle XRD patterns for all samples show only one broad

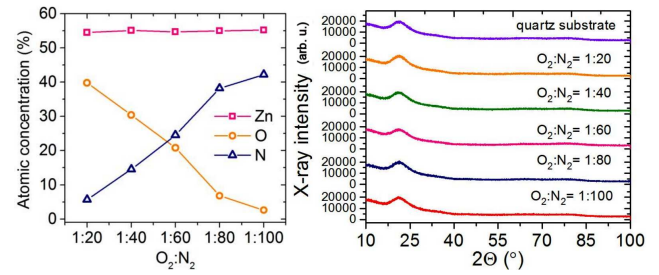


Fig. 2. Atomic composition (a) and diffraction patterns (b) of Zn-O-N films as a function of O₂:N₂ ratio.

peak at $2\Theta = 22^\circ$ corresponding to the quartz substrate, implying that all films have an amorphous or nanocrystalline microstructure.

Figure 3a shows resistivity and carrier concentration of the Zn-O-N films as a function of the oxygen to nitrogen ratio in the deposition atmosphere. All fabricated films were *n*-type semiconductors when characterized by the Hall measurements. The carrier concentration significantly increases from 1.2×10^{16} to as 3.4×10^{18} cm⁻³ as nitrogen content in sputtering plasma increases, indicating that oxygen may act as a carrier suppressor. The Hall mobility increases as the carrier concentration increases, which might be explained by the percolation model similar to the case of a-IGZO, and the Hall mobility above 80 cm²/(V s) was obtained at carrier concentrations equal to $n = 3.4 \times 10^{18}$ cm⁻³ (see Fig. 3b).

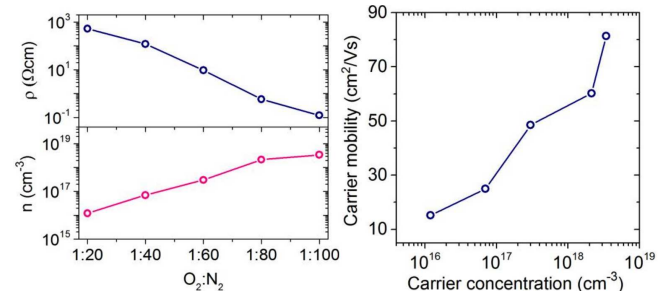


Fig. 3. Carrier concentration and resistivity of a-IGZO as a function of percentage of oxygen (a) and dependence of Hall mobility on the carrier concentration in a-IGZO (b).

It is noted that the Hall mobility of Zn-O-N increases with the carrier concentration more rapidly than for a-IGZO. This could be attributed to the relatively low potential barriers above the conduction band edge of Zn-O-N that is composed of single Zn 4s orbitals, unlike the random distribution of multiple cations (In, Ga, Zn) in a-IGZO.

The results of transmission measurements for different O₂:N₂ ratios are presented in Fig. 4a. It can be seen that a lower nitrogen content in the sputtering atmosphere yields higher transparency for the films in accordance with the formation of ZnO. The spectral characteristic curves show the enhanced absorption of light in

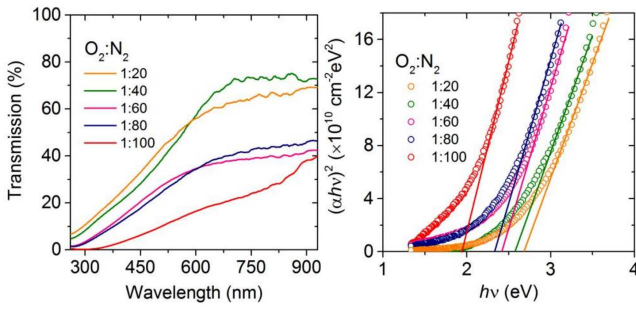


Fig. 4. Optical transmission (a) and Tauc plot (b) of Zn–O–N films deposited at various O₂:N₂ ratio.

the visible wavelength range. Optical bandgaps (E_{opt}) of fabricated materials were estimated from the Tauc model ($\alpha h\nu \propto (h\nu - E_{\text{opt}})^n$, where α is absorption coefficient, $h\nu$ is the photon energy, and $n = 2$ for allowed indirect transition) by extrapolation of linear Tauc's region to $(\alpha h\nu)^2 = 0$ [9]. Indeed, the evaluated optical bandgaps, presented in Fig. 4b, lie within the bandgap range of ZnO ($E_{\text{opt}} = 3.2$ eV) and Zn₃N₂ ($E_{\text{opt}} = 1.1$ eV), and monotonically decreases from $E_{\text{opt}} = 2.73$ eV for Zn₅₄O₄₀N₆ to $E_{\text{opt}} = 1.92$ eV for Zn₅₅O₃N₄₂. It is also noted that with increase of nitrogen content the Urbach tail decreases. Since the Urbach tail corresponds to the density subgap states, it suggests that the optical bandgap is narrowed as a consequence of elevation of valence band maximum above localized trap states (see Fig. 1), properly caused by the formation of Zn–N bonds which have smaller ionicity than Zn–O bonds [2, 5, 6].

4. Conclusions

Amorphous Zn–O–N thin films were fabricated by reactive rf magnetron sputtering and characterized by use of complementary methods of compositional and microstructural analysis. The oxygen to nitrogen ratio in the deposition atmosphere significantly affects the electrical properties of the films. In contrast to processes in which the reaction for either the oxide or the nitride

is dominant, the multireaction process yields a substantially amorphous films with the Hall mobility within the range from 15 to 80 cm²/(V s). The optical bandgap Zn–O–N is in the range of 1.92 eV to 2.73 eV. We attribute the enhancement of transport properties to the narrowing of E_{opt} by elevation of valence band maximum over native trap states localized in the lower band gap region. Chemical, transport and optical properties make Zn–O–N technology strongly promising to achieve high mobility required the realization of high-performance thin film transistors.

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