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On the zinc nitride properties and the unintentional incorporation of oxygen

C. García Núñez [*], J.L. Pau, M.J. Hernández, M. Cervera, E. Ruiz, J. Piqueras

Laboratorio de Microelectrónica, Departamento de Física Aplicada, Universidad Autónoma de Madrid, c/ Francisco Tomás y Valiente 7, 28049 Madrid, Spain

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ABSTRACT

Zinc nitride films were prepared by radio-frequency magnetron sputtering in N_2/Ar ambient using different substrates (glass and thermally-oxidized-Si) and buffer layers (low-temperature Zn_3N_2 and ZnO). Resonant Rutherford backscattering (RBS) allowed determining Zn_xN_y stoichiometry and thickness. Despite the sputtering system was operated in high vacuum conditions, unintentional oxygen incorporation during growth was detected. Calculations of the relative oxygen concentration showed that the oxygen content was very dependent on the growth rate. Ex-situ oxidation was also analyzed by resonant RBS and compared with the results of as-grown layers. Scanning electron microscopy and X-ray diffraction revealed that surface morphology and crystal orientation were strongly dependent on the substrate temperature (T_s). In addition, optical transmission measurements show a reduction of the optical energy band gap from 1.46 to 1.25 eV as T_s increased. The electrical properties were examined as a function of growth rate, total working gas flux and T_s aiming to maximize electron mobility. From those studies, it was found that Hall mobility increased significantly as the growth rate decreased. A maximum mobility of 100 cm^2/Vs and a minimum carrier concentration of 3.2×10^{18} cm^{-3} were achieved at a T_s of 423 K and a growth rate of 4.44 nm/min.

1. Introduction

Zinc nitride (Zn_3N_2) is recognized as a II–V semiconductor with promising electrical properties. Due to its high mobility, it is considered a good candidate to improve the efficiency of electronic devices such as thin film transistors (TFTs). These devices are mainly based on amorphous or polycrystalline Si whose properties commonly limit the performance of flat-panel displays. Zn_3N_2-based TFTs have been demonstrated in the past; however, their performance is still below average Si-based TFTs and improvement is needed [1]. Moreover, an interesting property of Zn_3N_2 is the possibility of transforming Zn_3N_2 into p-type ZnO by thermal annealing. The lack of a reproducible method to obtain p-type ZnO makes this procedure very attractive for the fabrication of p-n ZnO heterojunctions with application in ultraviolet and white lighting.

Depending on the growth technique and growth conditions used to synthesize Zn_3N_2, band gap values between 1.01 [2] and 3.4 eV [3] have been reported. Such a wide range of values is unusual in other semiconductors, so the origin of the discrepancy is still under debate. Electrical characteristics are slightly dependent on the growth technique. Futsuhara et al. carried out a study on the electrical properties of Zn_3N_2 films grown by radio-frequency (rf) sputtering under different N_2/Ar gas ratios, which showed n-type conduction and a maximum electron mobility of ~100 cm^2/Vs [4]. Mobility was mainly limited by both ionized impurity and grain boundary scattering processes. The highest mobility values reported to date have been achieved using metal organic chemical vapor deposition (MOCVD) (118 cm^2/Vs) and rf plasma-assisted molecular beam epitaxy (MBE) (156 cm^2/Vs) [5]. Those mobilities, along with carrier concentrations in the range of 10^{20} cm^{-3}, provide conductivity values which are slightly above those obtained in polycrystalline Si. Glass is a common substrate used for the deposition of Zn_3N_2 films which yields polycrystalline structures and prevents parallel conduction during electrical characterization. However, the effect of the substrate on the optical and electrical properties of Zn_3N_2 is still unclear.

In the past, those works including the analysis of the chemical composition of zinc nitride layers typically focused on the investigation of the nitride composition near the surface by using Auger electron spectroscopy and X-ray photoelectron spectroscopy [4–7]. From these studies, several authors showed oxygen contamination, which was attributed to spontaneous reaction after air exposure. The effect of oxygen impurities in the energy band diagram of Zn_3N_2 has also received special attention in theoretical works [8]. This work addresses the electrical, optical, compositional and morphological properties of zinc nitride layers prepared by rf-magnetron sputtering under different process conditions. In addition, it investigates the effects of oxygen impurities in Zn_3N_2 films grown by rf-magnetron sputtering. Two sources of contamination are identified: 1) oxygen contamination during growth (in-situ) and 2) oxygen contamination caused by long air exposure after growth (ex-situ). Oxygen concentration as a function of growth parameters is analyzed by means of resonant Rutherford backscattering (RBS). The effect of

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[*] Corresponding author. Tel.: +34 91 497 8607; fax: +34 91 497 4895.
E-mail address: carlos.garcia@uam.es (C.G. Núñez).

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oxygen contamination during growth on the electrical and optical properties of the layers is discussed.

2. Experimental details

Zn_3N_2 layers were synthesized from a pure Zn (99.995% purity) target using a mixture of N_2 (99.999% purity) and Ar (99.995% purity) as working gases. Each gas was introduced through its own mass flow controller. N_2 gas concentrations between 73% and 100% were used. To study the effect of growth temperature, deposition rate, and total gas flow, three series of samples were prepared on glass substrates keeping a constant chamber pressure of 1 Pa by adjusting the pumping rate with a throttle valve accordingly: a) samples grown at substrate temperatures (T_s) between 298 and 523 K, at 200 W and 30 sccm, b) samples grown at rf powers from 25 to 200 W, at 473 K and 30 sccm, and c) samples grown at total gas flows between 10 and 35 sccm, at 423 K and 25 W. In all cases, layer thicknesses ranged from 0.1 to 2.2 μm, as determined using a stylus profiler. The study was completed with the growth of samples on oxidized-Si substrates and the use of Zn_3N_2 and ZnO buffer layers of different thicknesses.

The samples, previously rinsed in acetone and ethanol, were introduced in the load chamber and placed in the substrate holder. After pumping down to 0.1 Pa, the substrate holder was transferred to the heating position in the main chamber. The main chamber was then reevacuated and the substrate holder heated up to the deposition temperature. Prior to deposition, the substrates were sputter cleaned with Ar to avoid unintentional surface impurities. Additionally, the target was also sputtered during five minutes before each growth.

Resonant RBS measurements performed at the Center of Microanalysis of Materials (CMAM/UAM) enabled calculation of the stoichiometries and thicknesses of the Zn_3N_2 layers through the use of the data fitting software SIMNRA. Resonant RBS studies were performed using alpha particles at energies of 3.045 and 3.7 MeV to enhance backscattered signals from O and N, respectively, through the nuclear resonances. The backscattered ions were detected by a standard Si-barrier detector located at an angle of 170° to the beam direction. The energy calibration of the detector was 2.62 keV/channel with an energy offset of 114 keV. Samples irradiated at 3.7 MeV produced a parasitic proton signal coming from the $^{14}N(\alpha,p_0)^{17}O$ reaction whose energy overlaps with the signal of the backscattered alpha particles in the $^{14}N(\alpha,\alpha)^{14}N$ reaction [9]. In order to subtract the contribution of protons from the backscattered signal, a 13-μm thick mylar foil was used in front of a second detector situated at 165°.

The morphology of the Zn_3N_2 samples was examined by scanning electron microscopy (SEM, Philips XL30) at 20-kV operation voltage. Crystal structure was investigated by grazing incidence X-ray diffraction (XRD) in a Siemens D-5000 (Cu $K_{\alpha}1 = 15.4059$ nm) system and using θ–2θ configuration. Transmission measurements were performed using a UV/Vis/NIR spectrophotometer in the 0.8–3.2 eV energy range.

Electrical properties such as resistivity (ρ), conduction type, carrier concentration (n) and mobility (μ) were determined by Hall Effect measurements using the four-probe Van der Pauw technique. Au contacts were evaporated at the four corners of each sample. The contacts presented ohmic characteristics as demonstrated by the linear *I-V* curves obtained between every pair of contacts. The resistance of these contacts ranged from 10^2 to 10^3 Ω which allow distinguishing small Hall voltage variations. The measurements were performed using thirteen different magnetic fields between −0.6 and 0.6 T (0.1 T step) and two different currents (10 and −10 mA), all of which provided equivalent results.

3. Results and discussion

RBS spectra were taken at alpha particle energies of 3.045 and 3.7 MeV. The signal backscattered from Zn atoms was easily identified in the high energy range of both spectra, as shown in Fig. 1 for a sample grown at 100 W and 473 K. The signal bandwidth accounts for the thickness of the Zn_3N_2 film being in good agreement with the growth rate estimated from profilometry. As mentioned above, to accurately determine the actual intensity of the RBS signal obtained from N atoms, it is necessary to subtract the proton contribution from the total signal at 1 MeV (Fig. 1(b)). After subtraction, the spectra were analyzed by SIMNRA software, allowing extraction of the Zn and N relative concentrations.

RBS measurements were performed on the sample series grown at different rf-powers and growth temperatures. The RBS analysis showed an O signal from the Zn_3N_2 film which increased from 1% to 16% as the rf-power reduced from 150 to 25 W (Fig. 2). Resulting O, N, and Zn contents for the rf-power sample series are included in Table 1. A low rf-power produced less active species in the plasma, and so the growth rate reduced from 50 to 3.8 nm/min. The RBS spectra showed abrupt interfaces between the substrate and the nitride layer in all the cases with no signs of contamination from the substrate. To fit the experimental results, a two-layer model based on a ZnO film atop the Zn_3N_2 was used to account for the formation of a native oxide layer on the surface after air exposure. In addition to this surface layer, the fitting works revealed high oxygen concentrations in the nitride films. A small amount of O_2 in the chamber produced effective O incorporation since the Zn-O bond is far more stable than the Zn-N bond. That can be easily explained in terms of the Pauling's analysis about the bond ionicity between two elements which is proportional to X_A–X_B, X being the electronegativity of each element. The electronegativity values for Zn, N and O using Pauling's scale are: 1.65, 3.04, and 3.44, respectively. Therefore, the bond ionicity of Zn-O is higher than the ionicity of Zn–N. Suda et al. used rf-plasma assisted MBE for the preparation of zinc nitride also observing oxygen contamination in the resultant layers attributed to oxygen generation in the quartz tube of

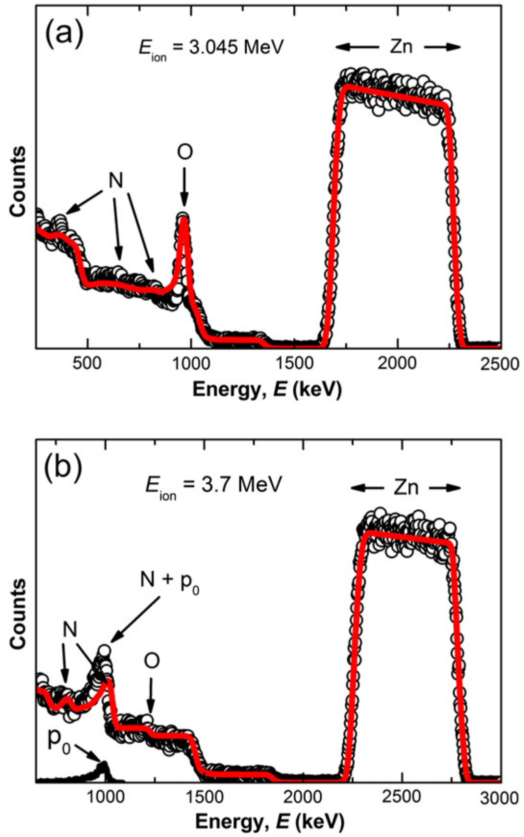

Fig. 1. Experimental (open black dots) and simulated (red line) data for a Zn_xN_y/glass sample (x = 3 and y = 2) at two different ion beam energies: (a) 3.045 and (b) 3.7 MeV.