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ELECTRICAL ENGINEERING -
DEVICES AND SYSTEMS,
MATERIALS AND TECHNOLOGIES
FOR THE FUTURE**

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Zinc Oxide - Unique Material for Micro- /Nanotechnology

1. INTRODUCTION

Zinc oxide (ZnO) is a unique material that exhibits semiconducting, piezoelectric, pyroelectric and optoelectronic multiple properties. Zinc oxide is a transparent semiconductor with a direct bandgap of 3.37 eV and large excitation binding energy (60 meV), and exhibits near-UV emission and absorption, as well as high transparency and natural n-type in conductivity. Pure ZnO crystallizes in the hexagonal (wurtzite) system with lattice parameters $a = 0.326$ nm and $c = 0.520$ nm. The structure of ZnO can be simply described as number of alternating planes composed of tetrahedrally coordinated O^{2-} and Zn^{2+} ions, stacked alternately along the c -axis (Fig. 1.) [1]. High electron carrier densities in undoped ZnO have been attributed to the native defects in ZnO structure such as zinc and oxygen vacancies, zinc and oxygen interstitials, and zinc and oxygen antisites. Electrons from the native defect zinc interstitials, a double donor, are the dominant carriers for zinc-rich conditions.

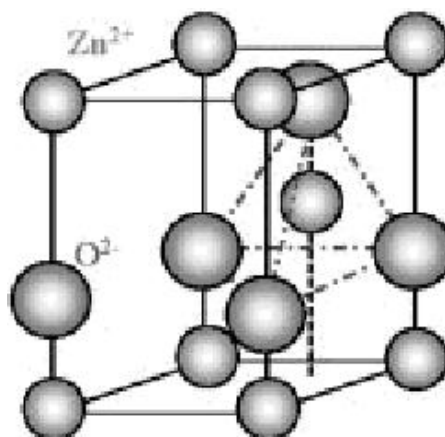


Fig. 1. Wurtzite structure model of ZnO with tetrahedral configuration

Recently, zinc oxide has attracted much attention because of wide applications in optoelectronic devices (short wavelength light emitting and detecting devices), surface and bulk acoustic wave devices, piezoelectric transducers, gas sensing and solar cells [2]. The semiconducting nanostructures such as nano-/fibers, wires, rods, tubes, belts, saws, springs, rings, bows and

propellers have caught considerable attention due to zinc oxide great application potential in nanoactuators and nanosensors [3]. The highly one-dimensional ZnO nanostructures were realized using various methods such as vapor transport and deposition, thermal decomposition [4] and evaporation [5] (e.g. vapor liquid solid (VLS) process [6], metal-organic chemical vapor deposition (MOCVD) [7]).

ZnO thin film deposition by sputtering is determined by complex processes proceeding: (a) at the target bombarded by energetic ions, (b) in the low-temperature plasma, (c) on the surface of substrate and growing film. In general, thin film growth is influenced by the kinetic energy of coating species on the substrate – in addition to substrate temperature a total energy flux is acting to the substrate and growing thin film. It depends mainly on the amount and the energy of: (i) sputtered coating species, (ii) energetic neutral working gas atoms (neutralized and reflected at the target), (iii) energetic secondary electrons emitted from the target, (iv) negative ions coming from the working gas plasma or target, (v) ions bombarding the substrate in bias or reactive mode. RF sputtering is capable: a low -temperature ion – assisted deposition of metals, semiconductors, insulators, the before/post deposition modification of substrate/thin - film surface by ions on the micro-/nano- level; change of deposition rate in wide range (0,1 to 10 nm/s); to control further parameters which are important for thin film growth (substrate temperature, plasma density, composition of working gas, ion bombardment of film during deposition). In addition there is a significant contribution of secondary electron bombardment to the atomic scale heating of the film when it is prepared by the RF diode sputtering.

We have done the systematic investigation of ZnO thin films prepared by RF diode sputtering from point of view their application in sensors and actuators.

EXPERIMENTAL PROCEDURE

The Au/ZnO structures were RF diode sputter deposited on Si and Corning glass substrates using a ZnO target (99.99 % purity, in 20 cm diameter) and metal Au target (99.95 % purity, in 20 cm diameter). The substrates were cleaned by standard chemical method. The sputtering chamber was pumped down to 10^{-5} Pa before admission of the sputtering gas Ar (99.9995 %) and total gas pressure 1.3 Pa was kept constant. The morphology of Au and ZnO structures was characterized using scanning electron microscope SEM LEO 1550 and atomic force microscope AFM Topometrix TMX 2010. The crystal orientation and microstrains of the films were investigated by an automatic powder X-ray diffractometer AXS Bruker D8 with Eulerian cradle

and 2D detector (CoK α , $\lambda = 0.179$ nm). The resistivity and carrier concentration in ZnO films were obtained from Van der Pauw measurements.

RESULTS AND DISCUSSION

A. Semiconducting n- and p- type ZnO thin films

Non-stoichiometric ZnO_{1-x} thin films sputtered from ZnO target in pure Ar gas exhibited disordered grain structure with orientations of <100>, <002> and <101> (Fig 2.). The set of two-dimensional diffraction patterns displays three Debye rings of ZnO Bragg reflections (Fig. 3.). The white circle is a Laue spot diffracted by substrate material (c-Si) due to the continuous X-ray radiation. ZnO_{1-x} resistivity was sensitive to presence of oxygen and we used it in planar resistance gas sensor with TiN thin film heater and temperature sensor.

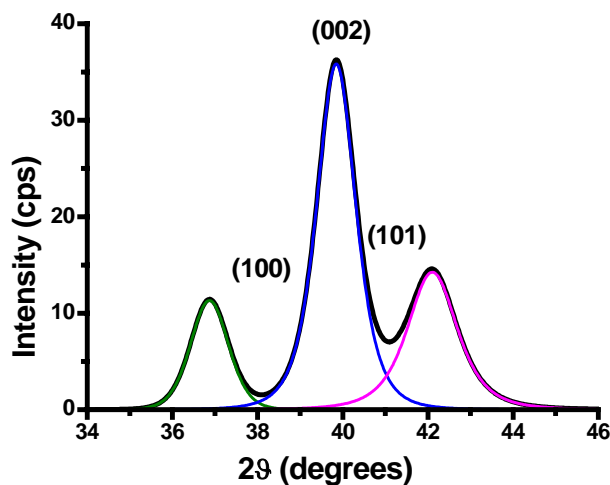


Fig 2. Sputtered ZnO thin films showed columnar polycrystalline structure with preferred orientation in <002> direction

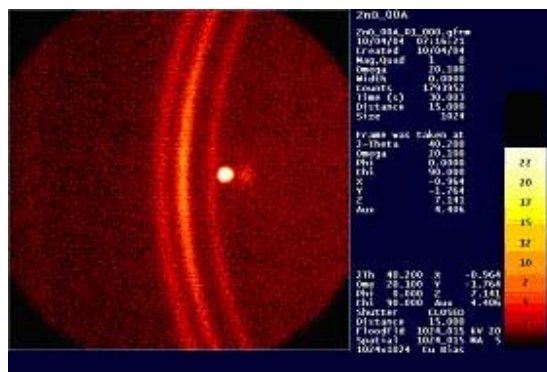


Fig 3. Two dimensional diffraction pattern of ZnO film

Reactive sputtering in Ar+O₂ working gas (up to 75 % of O₂) at substrate temperatures T_s = 20 °C and 300 °C improved the structure progressively from more disordered fibrous ZnO grains to columnar crystallites preferentially oriented along c-axis normally to the substrate (<002> direction). The n-type resistivity was slightly dependent on the RF power, ρ = 0.4 ÷ 1.0 Ωcm, transparency in VIS region was 85 % with adsorption edge in near UV region 3.33 eV which is close to the bandgap of bulk ZnO E_g = 3.37 eV.

ZnO exhibits intrinsic n-type conductivity and can easily be n-type doped but it turned out to be more difficult to fabricate low-resistivity p-type ZnO. Nitrogen doping is considered an effective method to realize p-type ZnO:N thin films [8]. Novelty of our approach is in use of plasma assisted deposition method – RF diode sputtering – which allow to perform direct action of ions, ion complex and electrons on growing film with the aim to form suitable N_O -O acceptors. ZnO:N thin films were prepared by RF diode sputtering from ZnO target in different content of N₂ (0÷100%) in sputtering Ar gas on Corning glass substrates. The p-type conductivity of ZnO:N films was obtained by deposition in sputtering gas with N₂ contend higher then 25 %. X-ray diffraction measurements (XRD) showed that ZnO:N films had the preferential orientation of (002) plane at 25 % N₂ and of (100) plane for higher N₂ concentrations (Fig. 4).

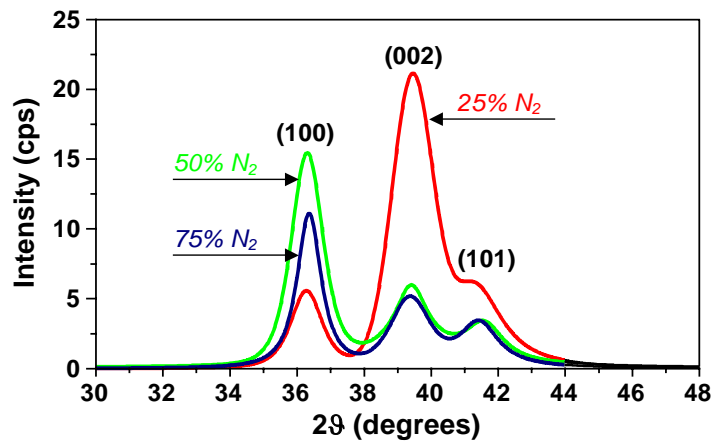


Fig. 4. XRD patterns for ZnO films doped with different percentage of N₂ in sputtering gas

The average grain size was from 7 to 42 nm for all Ar/N₂ ratios and average microstrains were relatively high (10×10^{-3}). The p-type conductivity of our ZnO thin films can be attributed to the presence of NO molecules, which will introduce low-formation energy N_O, which is an acceptor in ZnO [9]. The electrical properties of n-doped ZnO thin films as a function of nitrogen percentage in Ar/N₂ sputtering gas are shown in Fig. 5 a, b.

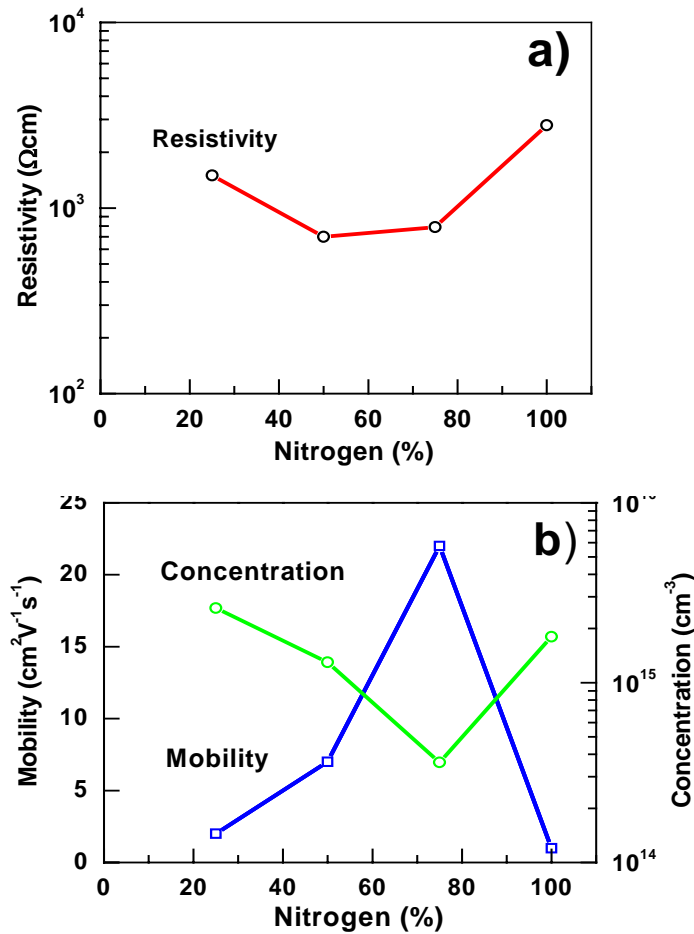


Fig. 5. Dependence of a) resistivity, b) Hall mobility and carrier concentration on nitrogen percentage for as grown ZnO:N films

The film's resistivity decreases with the increase of the percentage of nitrogen from 25 % to 75 %. The minimum value of resistivity of $790 \Omega\text{cm}$, a carrier concentration of $3.6 \times 10^{14} \text{ cm}^{-3}$ and the Hall mobility of $22 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ were yielded at 75 % N_2 . The further increase of nitrogen percentage in the sputtering gas from 75 % to 100 % leads to the increase of the resistivity. The lowest resistivity is a result of the high mobility. The highest carrier concentration $P \sim 2.6 \times 10^{15} \text{ cm}^{-3}$ is recorded for 25 % N_2 in the sputtering gas. The strong dependence of the electrical properties of sputtered ZnO:N films on dopant content can be explained with the different scattering mechanism of free carriers. Films with small dopant content exhibit good crystal structure in terms of grain size and grain orientation. The dopant atoms are effectively incorporated in the ZnO lattice but their concentration is low. Thus ionized impurity scattering becomes dominant in comparison to grain boundary scattering. Hence a low carrier mobility and a low hole concentration were obtained at samples deposited with 25% N_2 in the sputtering gas. The increasing of the dopant content in ZnO films introduce furthers scattering centers and thus the decrease of carrier concentration at high dopant levels. The increase of the carrier

concentration in films deposited at 100% N₂ in the sputtering gas can be a result of the high concentration of NO incorporated into the films. The compensation effect by N₂ molecules at O sites ((N₂)_O) and N_O - (N₂)_O complexes can be responsible for non-stable conductivity types of the film deposited at 50% N₂ in the sputtering gas.

B. Nanostructured surface of ZnO thin films

Our second target is to form of nanostructured surfaces of ZnO thin films (nanoscale roughness, nanofibres). For growth of nanostructures are dominant initial growth phases: seed formation, nucleation growth of clusters and islands and their coalescence. Schematic simplified growth of ZnO structures (nanodots, nanofibers) on Au particles is shown on Fig 6. The nanofibre growth requires the aid of catalyzing metal particles, which are of gold in our case. Therefore, it is key to be able to accurately control the position and size of the seed Au particles during growth. RF diode sputtered Au nanoparticles of mean diameter of 10th nm (Fig. 7.) were as seeds for growth of nanostructured surface of ZnO thin films in thickness of 200 nm (Fig. 8.).

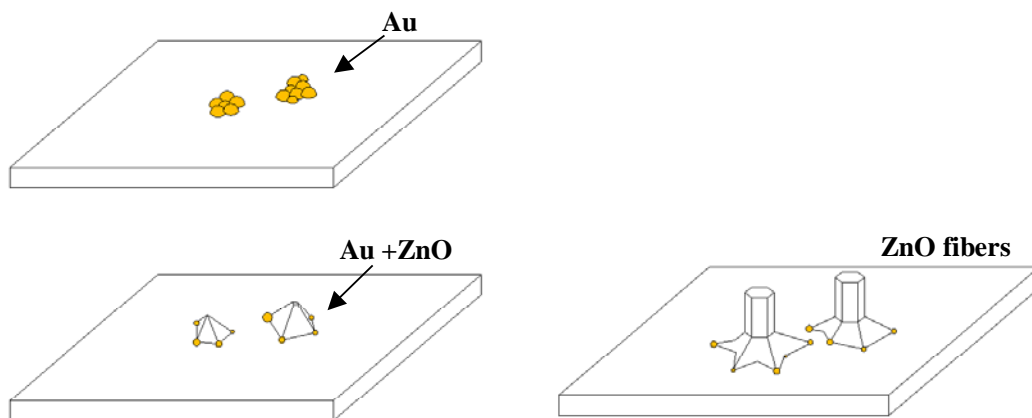


Fig. 6. Schematic illustration of the nanostructure growth of the ZnO

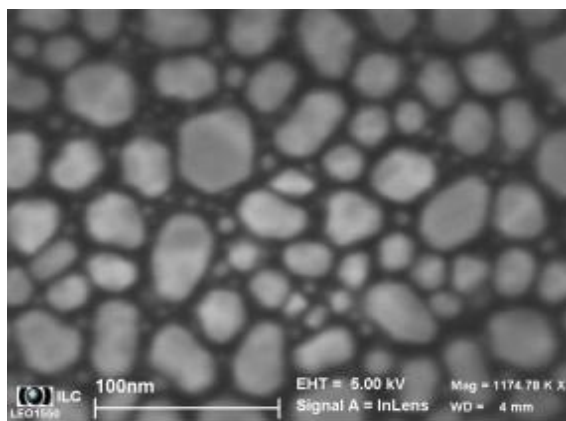


Fig. 7. Au nanoparticles deposited by RF sputtering on Si substrate

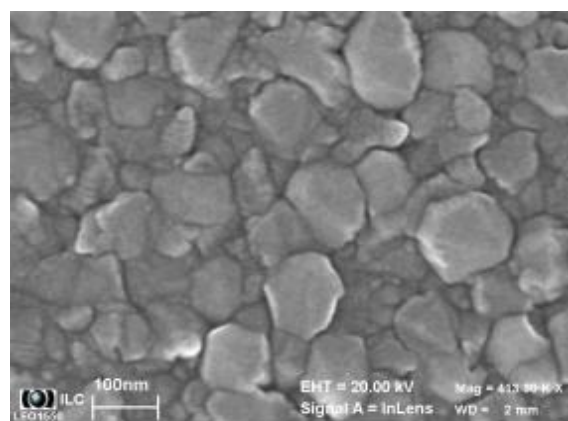


Fig. 8. Nanostructured surface of ZnO thin film

Next we formed nanostructured surface ZnO by using different bias voltage on the substrate (0 to -175V) (Fig.13.) during deposition at two different voltages on the target (Fig. 9, 10, 11). Microroughness of ZnO surfaces were measured by AFM (Root Mean Square roughness), maximal value (10 nm) was reached by -175 V bias sputtering. The use of lower target voltage ($V_{\text{Target}} = -300\text{V}$, Fig. 11) caused smoother surface of the thin film. More roughness surface of the thin film was at high target voltage ($V_{\text{Target}} = -900\text{V}$, Fig. 10) due to atomic scale heating of the film during deposition. Influence of different amount of Ar ions and their kinetic energy on surface structure of films sputtered bias voltages is shown on Fig. 13.

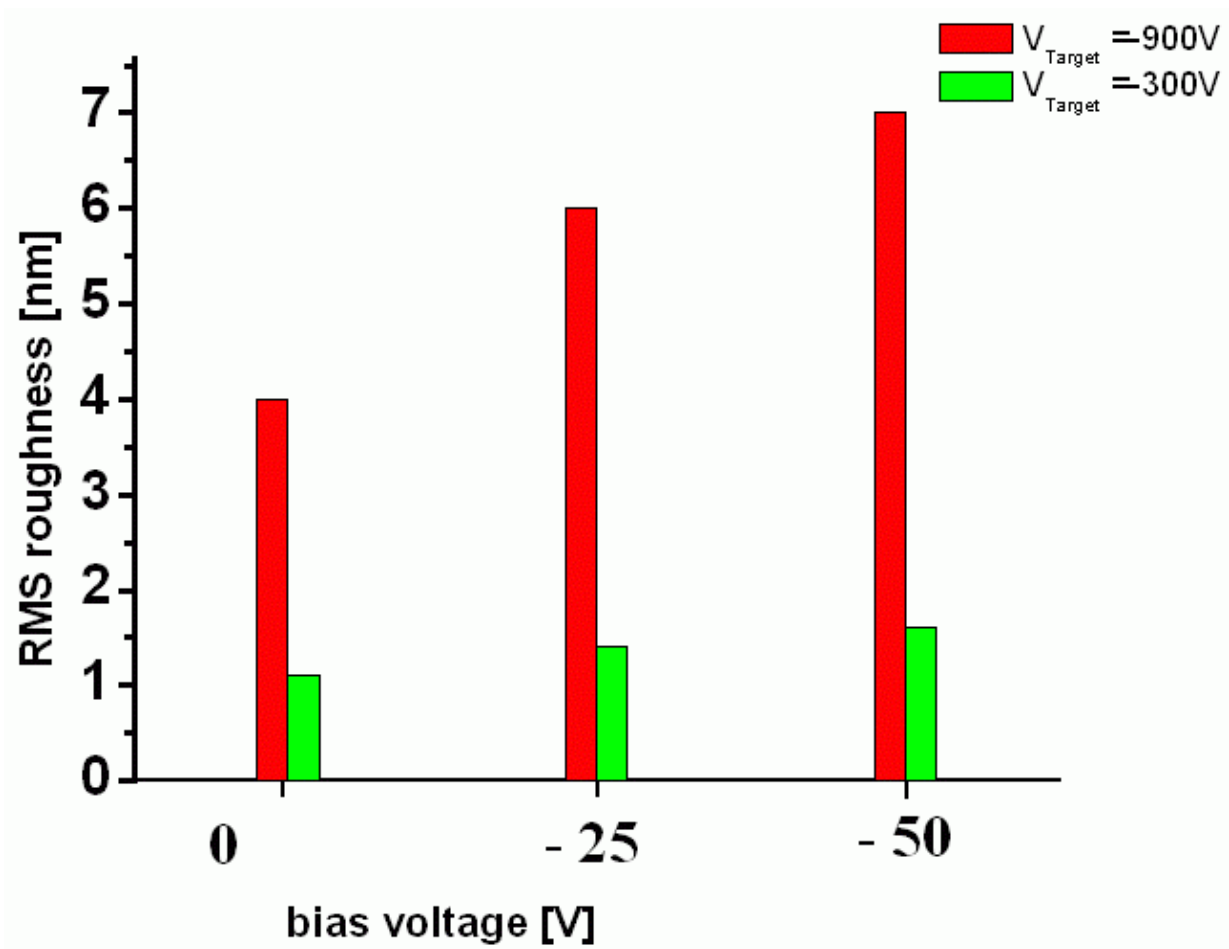


Fig 9. Sputtered ZnO by using different bias voltage (0 to -50V) during deposition at two target voltage ($V_{\text{Target}} = -900\text{V}$, $V_{\text{Target}} = -300\text{V}$)

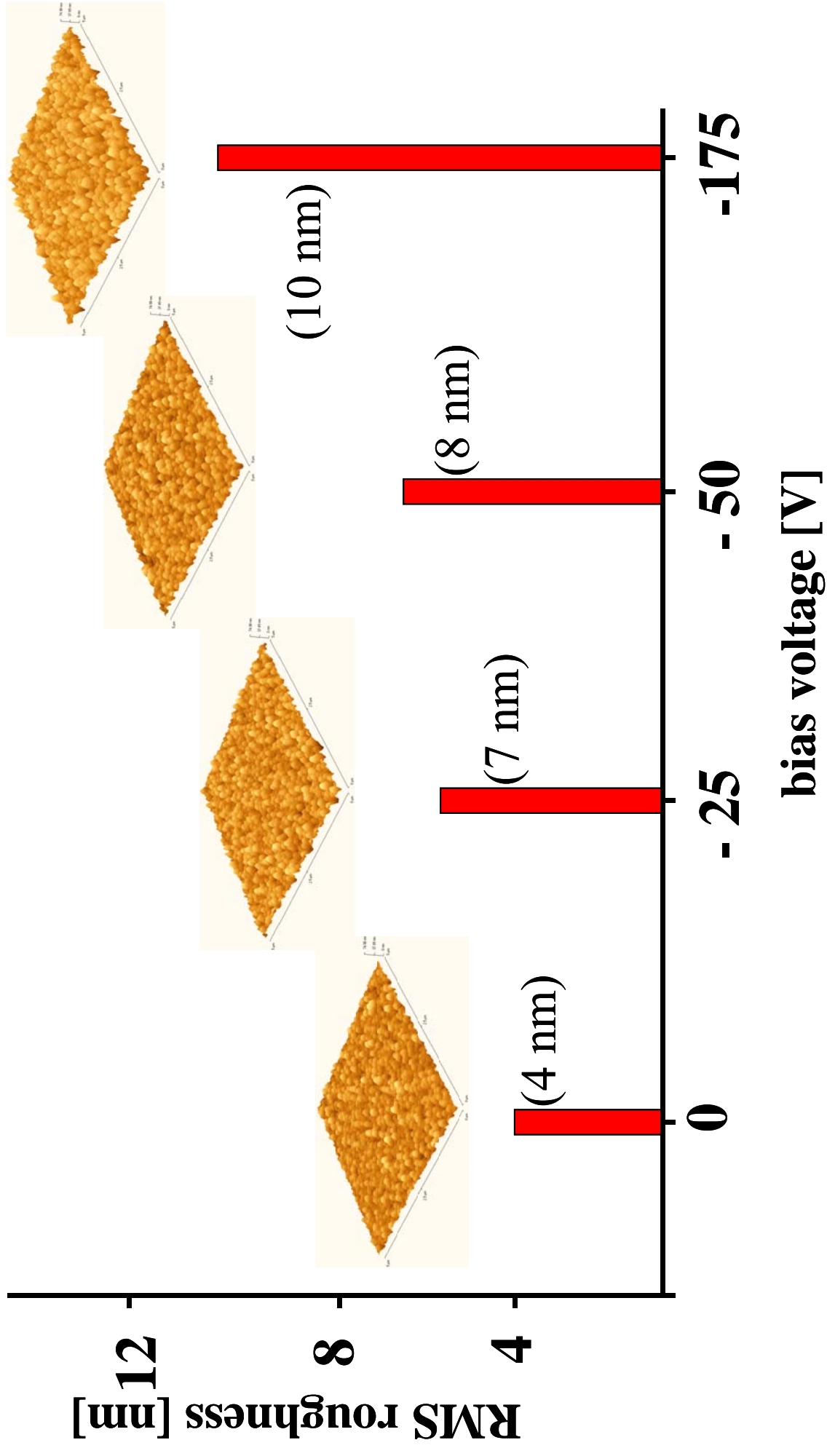


Fig.10. Sputtered ZnO by using different bias voltage (0 to - 50V) during deposition, $V_{\text{Target}} = -900\text{V}$

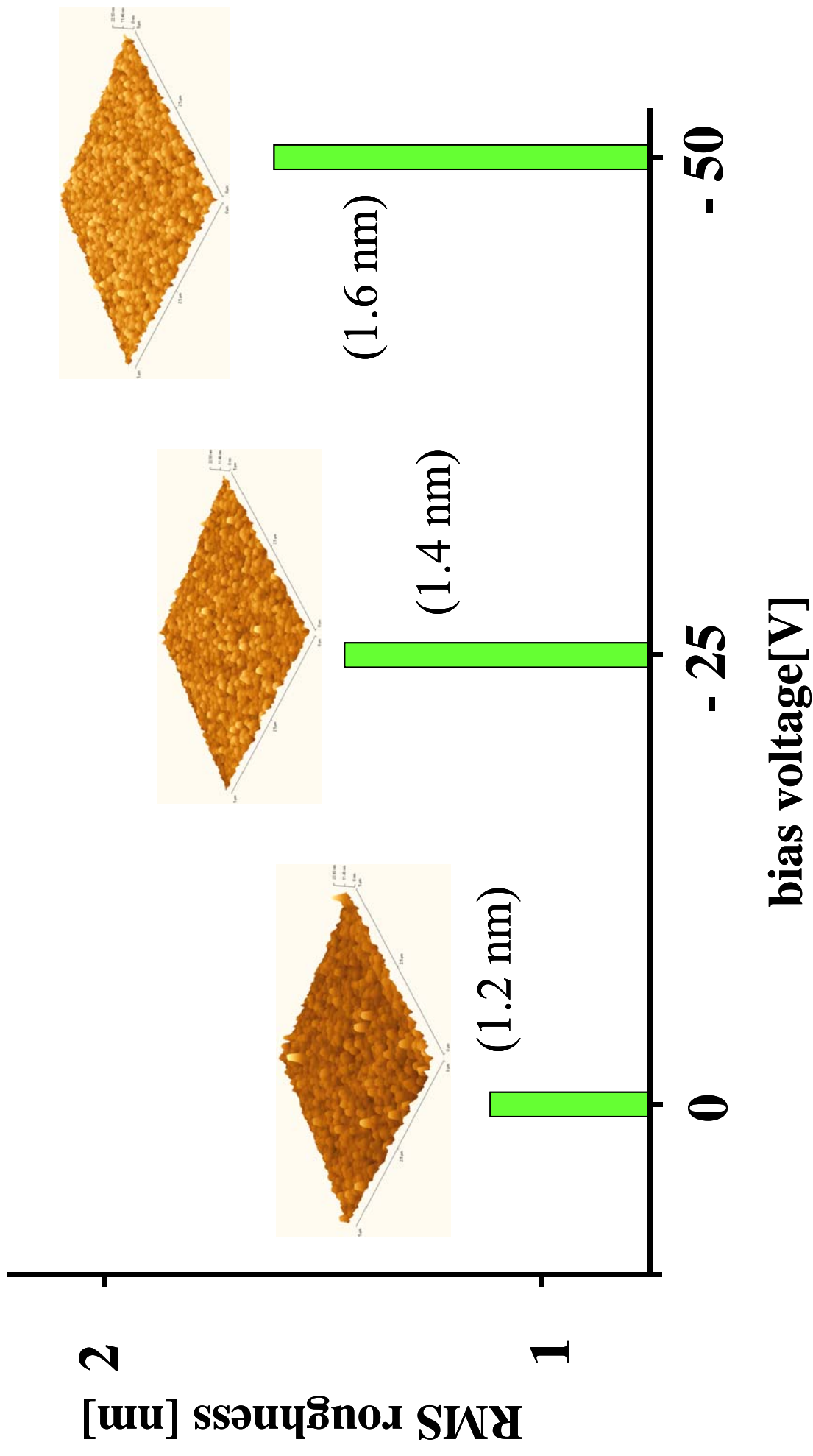


Fig.11. Sputtered ZnO by using different bias voltage (0 to -50V) during deposition, $V_{\text{Target}} = -300\text{V}$

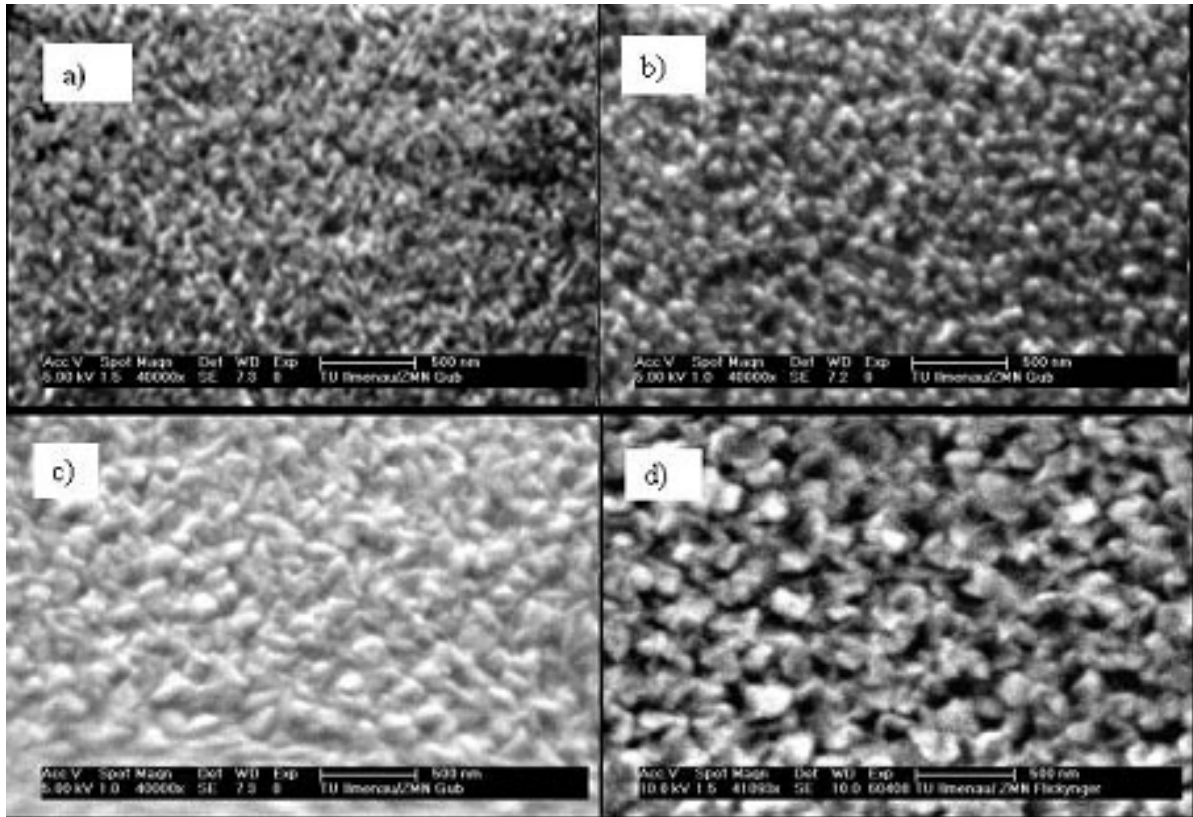


Fig. 13. The ZnO nanostructured surface by RF diode sputtering, $V_{\text{Target}} = -900\text{V}$:
 a) Bias = 0V, the 44.6° tilted view, b) Bias = - 25V, the 45° tilted view,
 c) Bias = - 50V, the 43.8° tilted view, d) Bias = - 175V, top view

CONCLUSIONS

We synthesized p-type ZnO thin films on Corning glass substrate using nitrogen as a dopant by RF diode sputtering. Sputtering is deposition process conditions of which significantly differ from thermodynamic balance. Therefore we can expect that p-type properties of RF sputtered ZnO:N films will be metastable and highly dependent on nitrogen content in sputtering gas. In order to improve p-type properties of ZnO thin films will be necessary to combine nitrogen doping with other co-dopants (e.g. Al).

ZnO offers the broad spectrum of unique physical and chemical properties, what is getting it into group of the most important nanomaterials for integration with microsystems and biotechnology. Our preliminary results have confirmed that sputtering is one of available deposition method for forming of chosen ZnO nanostructures. Future target is to use of nanostructured surfaces of ZnO thin films for modern DNA-based biosensors.

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