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Characterization of sputtered NiO films using XRD and AFM

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Nickel oxide (NiO) is an attractive material for use as an antiferromagnetic layer [1], *p*-type transparent conducting films [2], in electrochromic devices [3, 4] and as a functional sensor layer for chemical sensors [5]. In the bulk, NiO has a cubic (NaCl-type) structure with a lattice parameter of 0.4195 nm. NiO is considered to be a model semiconductor of hole-type conductivity. These films have been fabricated by various physical and chemical vapor deposition techniques such as reactive sputtering and plasma-enhanced chemical vapor deposition because chemical stability of the layers as well as their optical and electrical properties are excellent [6].

It is well known that the structural properties and surface morphology of materials in thin film form depend on the deposition techniques, deposition conditions and post-deposition processing. These properties for metal oxide films have become of great interest in the last few years. In particular, the field of gas sensors has benefited from the production of materials characterized by a high surface to volume ratio [7]. The gas-sensing properties of metal oxides are more or less related to the material surface, its high porosity and the microstructure with small particle size. In this case, the microstructure together with the chosen operation mode determine how the recognition of a gas at the sensor surface is transduced in one or several output signals. Also, the interaction of compact and porous layer with surrounding gases is rather different [8]. Porous layers are accessible to gases in the whole volume whereas compact films only interact with gases at the geometric surface. The gas active surface of porous layers is therefore much larger than in the case of compact layers.

In this letter, the effect of the process parameters and post-deposition annealing on the microstructure and the surface morphology of NiO thin films is reported. Throughout these investigations, the aim was to find the correlation between process parameters and these physical properties.

The NiO films were deposited by DC reactive magnetron sputtering from a Ni target (101.2 mm in diameter, thickness of 3 mm, and 99.95% pure) in a mixture of oxygen and argon onto unheated Si substrates. The distance between the target and the substrate was approximately 75 mm. A sputtering power of 600 W was used. Both argon inert flow and oxygen reactive flow were controlled by mass flow controllers. The relative partial pressure of oxygen varied from 20 to 60%. The total gas pressure was kept at 0.5 Pa. NiO films were prepared in two operation modes: metal-sputtering mode and oxide-sputtering mode. Details of these modes have been given elsewhere [9]. The sputtering conditions are listed in Table I. The film thickness under the above conditions was ranged from 100 to 150 nm and was measured by a Talystep. The crystal structure was identified with a Theta Theta Diffractometer D 5000 with a Goebel mirror in Bragg-Brentano geometry with Cu K_α radiation. The structure refinement process was calculated using the program POWDERCELL [10]. The surface morphology was observed by atomic force microscopy (AFM) using a Topometrix Discover TM 2000 under normal air conditions. In our case a 70 μm *x*, *y*, *z* linear scanner with *z*-resolution of 0.2 nm was used. After deposition, the films were annealed in a tube furnace for 8 h in dry air at 500 to 900 °C.

Fig. 1a presents the XRD diffraction patterns of the samples that were prepared at different oxygen contents in the working gas. From XRD spectra of as-deposited NiO films it was found that the NiO films prepared had both amorphous and polycrystalline structures. In the diffraction pattern from as-deposited samples in the oxide-sputtering mode, no diffraction peaks were observed. These films are X-ray amorphous. On the other hand, the diffraction patterns from other samples prepared in the metal-sputtering mode show the presence of diffraction peaks from the (111), (200) and (220) lattice planes of the NiO lattice. Peak positions are present at angles smaller by around 0.7–1.2 degree, which means a bigger distance between the lattice planes than

TABLE I Sample preparation conditions

Sample	8	6	7	9	10	11
Sputtering mode	Metal	Oxide	Oxide	Metal	Oxide	Oxide
Pumping speed (l/s)	275	275	275	136	136	136
Oxygen flow (sccm)	50	70	90	20	30	40
Oxygen content in working gas (%)	20	30	40	36	44	60
Average target voltage (V)	329	299	309	366	301	308

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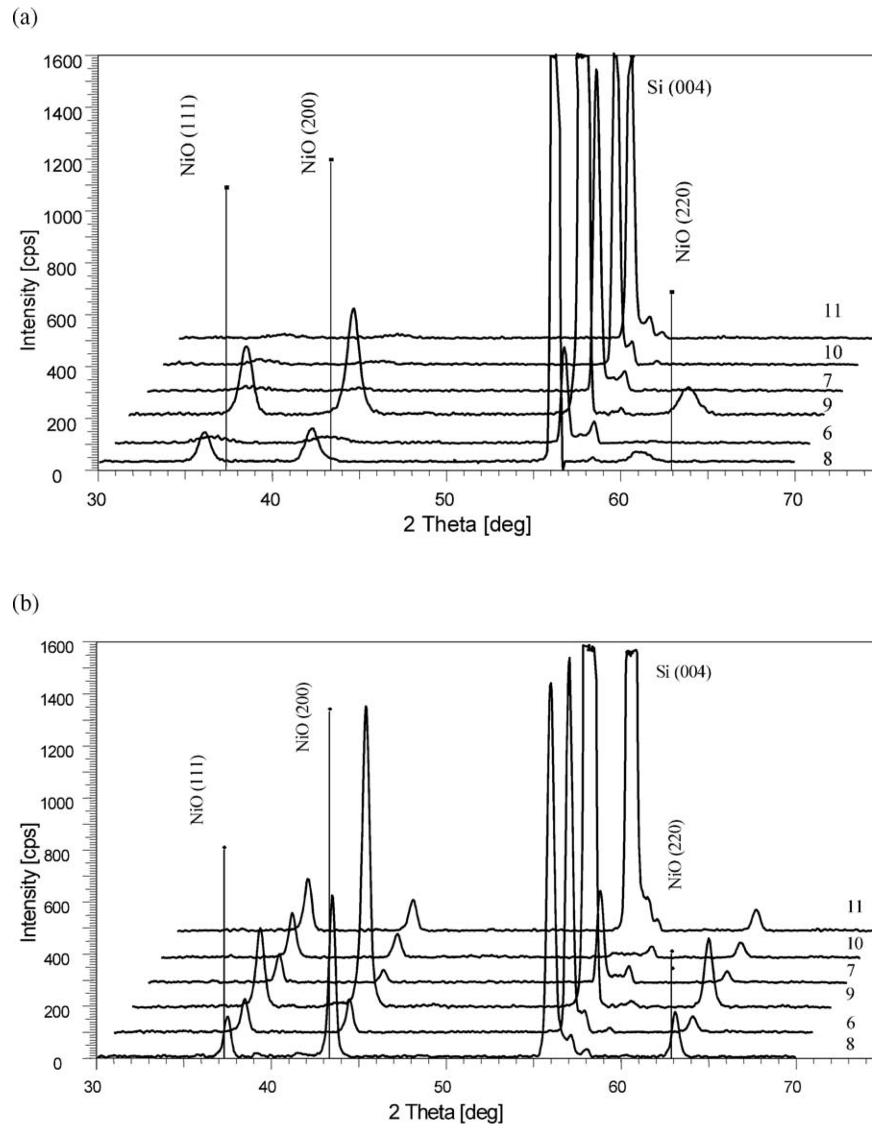

Figure 1 XRD patterns of (a) as-deposited NiO films and (b) annealed at 700 °C for 8 h in dry air prepared in the metal-sputtering mode (samples 8 and 9) and the oxide-sputtering mode (samples 6, 7, 10, 11).

expected in theory. We suggest that the observed amorphous structure in the oxide-sputtering mode and a polycrystalline structure in the metal-sputtering mode are connected with the NiO deposition conditions. As we can see in Table I, the metal-sputtering mode is characterized by high target voltages (329 and 366 V), while low target voltages (299–309 V) correspond to the oxide-sputtering mode. However, different results have also been reported. Sato *et al*. [2] found two weak diffraction peaks from the (111) and the (200) planes for NiO thin films deposited with the oxygen content above 20% by rf magnetron sputtering. Fujii *et al*. [6] observed NiO films with good crystallinity and (100) preferred orientation at substrate temperature of 150 °C and above. According to Kumagai *et al*. [5] the NiO films prepared by controlled growth with sequential surface chemical reactions had an amorphous structure. These different results indicate that the NiO film structure depends on the oxygen content as well as on the deposition method.

The effect of annealing temperatures on the structure of films is as follows. Fig. 1b shows the examples after annealing at 700 °C. The samples prepared in metal-sputtering mode become fully polycrystalline but the structure of the samples formed in the oxide-sputtering mode changes from amorphous to polycrystalline (fcc NiO phase). It was found that the samples prepared in the metal-sputtering mode had a strong (200) diffraction peak, which indicates a preferred orientation along [100] direction. As the annealing temperature is increased, its intensity increases. On the other hand, samples prepared in the oxide-sputtering mode show a strong (111) diffraction peak and its intensity also increases with increasing annealing temperature.

It was possible to calculate the texture grade (TC). This can be done with the theoretical intensities, given from JCPDS-file 4-835, cubic NiO. The strongest peak is the (200) with $I_o = 100\%$, (111) with $I_o = 91\%$ and (220) with $I_o = 57\%$. Using Equation 1 and in our case $k = 3$ the results of texture grade can be seen in Fig. 2.

$$\mathrm{TC}_{\mathrm{I}_{(\mathrm{hkl})}} = \frac{\frac{I_{(\mathrm{hkl})}}{I^0_{(\mathrm{hkl})}}}{\frac{1}{k}\sum_{\mathrm{i}=1}^{k} \frac{I_{\mathrm{i}_{(\mathrm{hkl})}}}{I^0_{\mathrm{i}_{(\mathrm{hkl})}}}} \tag{1}$$

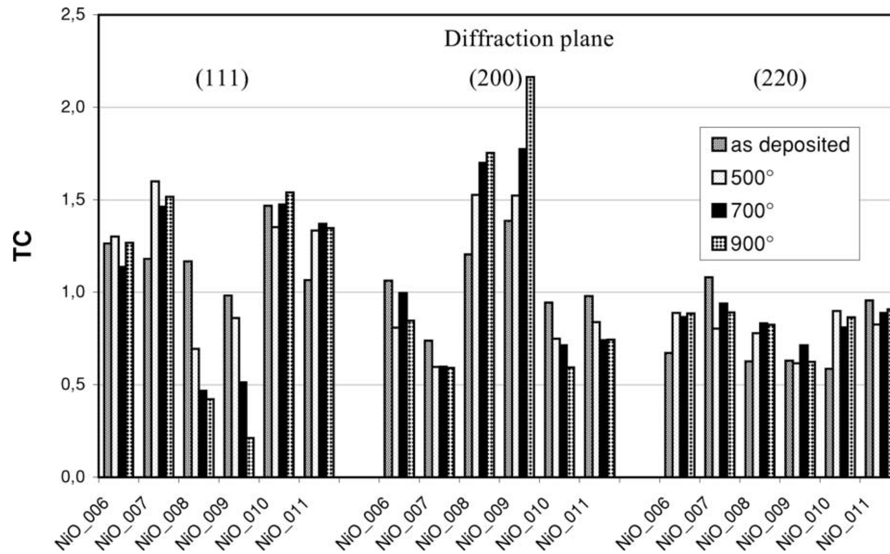

Figure 2 Calculated texture grade of as-deposited and annealed NiO films prepared in the metal-sputtering mode (samples 8 and 9) and the oxide-sputtering mode (samples 6, 7, 10, 11).

A texture grade equal to one for each peak means that the sample is an ideal polycrystalline material. The differences from one indicate a texture nature [11]. Values greater than one mean that in this direction a texture can be found. For lattice planes with values smaller than one it means there is a depletion of grains in this direction.

All X-ray peaks show a shift in their position. A fit between the measured positions and real lattice size was not successful for cubic (fcc) NiO. As a additional phase, rhombohedral NiO in hexagonal form was found in the JCPDS-database (see Table II). This rhombohedral phase leads to diffraction planes at the same positions as the cubic phase (see Table II). Using this rhombohedral cell, it was possible to fit the measured XRD diagrams and to obtain new lattice cell parameters. Fig. 3 shows these results. In a-direction, the changes in lattice parameters are smaller than in c-direction. More changes in lattice parameters are found in the metallic mode sputtering than in the oxide mode sputtering.

TABLE II XRD peak positions for cubic and rhombohedral NiO

Nickel oxide NiO					
f.c.c. Fm3m (225) JCPDS-No.: 4-835			Rhombohedral R-3m (166) JCPDS-No.: 44-1159		
$d_{(hkl)}$ (nm)	I	hkl	$d_{(hkl)}$ (nm)	I	hkl
0.24100	91	111	0.24120	60	101
0.20880	100	200	0.20885	100	012
0.14760	57	220	0.14773	30	110
			0.14761	25	104

TABLE III The average of the roughness of NiO films deduced from AFM analysis

Sample temperature (°C)	8		6	
	R (nm)	RMS (nm)	R (nm)	RMS (nm)
As-deposited	0.15	0.21	0.26	0.33
500	0.46	0.65	0.24	0.30
700	1.56	1.98	0.53	0.69
900	2.00	3.29	0.71	0.90

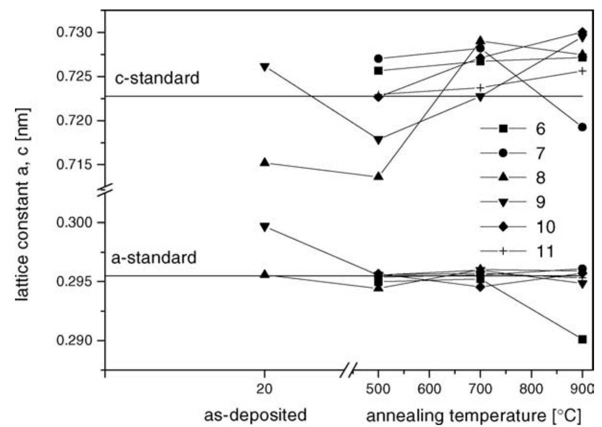

Figure 3 Calculated lattice constant for NiO films prepared in the metal-sputtering mode (samples 8 and 9) and the oxide-sputtering mode (samples 6, 7, 10, 11), rhombohedral type.

The AFM topography of the as-deposited NiO films prepared in both modes reveals that the film surface is rather smooth and compact. AFM observations, Fig. 4, show clear grains after annealing at a temperature of 700 °C. In XRD diagrams no changes of peak size between 700 and 900 °C are shown. This also indicates that the grain growth is completed at 700 °C annealing. The AFM results (Table III) also show that the values of the mean roughness R and the root mean square (RMS) for the sample prepared in the metal-sputtering mode are higher than in the oxide-sputtering mode. Besides these, in all our experiments it appeared that the surface roughness and the RMS increased with the increase of annealing temperature.

A more detailed study of NiO thin films as a perspective gas sensitive material is the scope of our present research. However, it can be concluded that only the as-deposited films in the metal-sputtering mode are crystalline and annealing in dry air leads to the formation of crystalline phases in all samples. During the annealing process changes in lattice sizes occur. The cubic cell NiO is distorted to a rhombohedral cell. It was only possible to fit the changes in lattice size experimentally

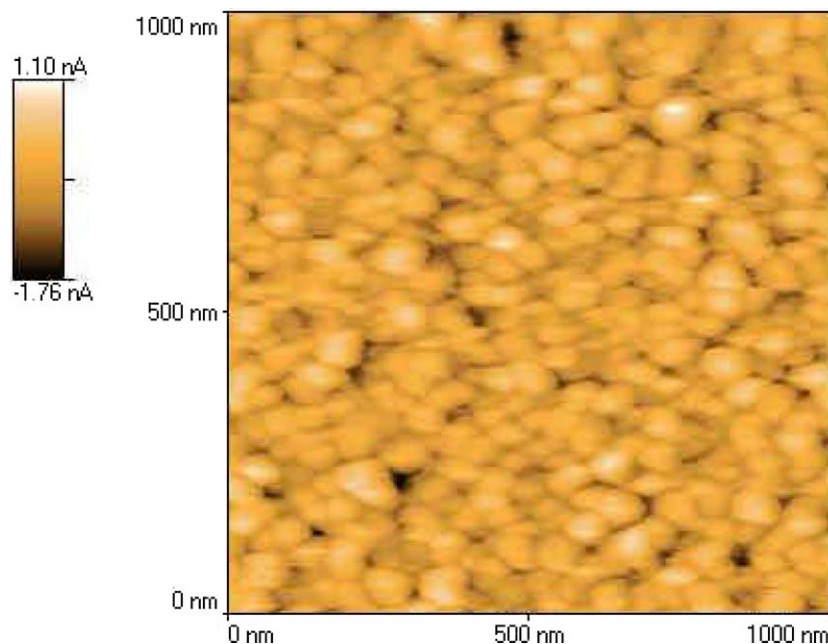

Figure 4 AFM images showing the surface (1×1 μm^2) of sample 6 prepared in oxide-sputtering mode after annealing at 700 °C.

using the rhombohedral form of the NiO crystal. The metallic mode sputtering leads to a surface with higher roughness.

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