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Electrical and optical properties of NiO films deposited by magnetron sputtering

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Films of transparent semiconductors are widely studied and developed because of high potential applications in electronics in last decade. Our work concerns the properties of NiO films fabricated by RF magnetron sputtering. Electrical and optical parameters of the films were characterized using Hall and transmittance measurements, respectively. *P*-type conductivity of as-deposited films and after annealing in oxygen or argon at the temperature range from 300 °C to 900 °C was verified. Transmittance of NiO films strongly depends on deposition temperature and oxygen amount during sputtering. Films deposited at room temperature without oxygen have transmittance near 50% in the visible range and resistivity about 65 Ωcm. An increase in oxygen amount in deposition gas mixture results in higher conductivity, but transmittance decreases below 6%. Resistivity of 0.125 Ωcm was attained at sputtering in oxygen. Films deposited at temperature elevated up to 500 °C are characterized by transmittance above 60% and lower conductivity. Annealing of NiO films in Ar causes resistivity to rise dramatically.

Keywords: transparent conductive oxide, NiO, *p*-type semiconductor, optical transmittance.

1. Introduction

Nickel oxide (NiO) is a semitransparent *p*-type semiconducting material with band gap width of about 3.8 eV [1]. It shows attractive electric [2], electrochromic [3] and thermoelectric [4] properties as well as high chemical resistance. It is used as gas sensors [5] or developed to fabricate photodetectors [6]. Lately there has been a lot of interest in nickel oxide's optical and electrochromic properties connected with its possible application in displays and "smart windows". Especially semiconducting NiO films would be usefully applied in UV detection [7], if these could reveal both satisfactory transmittance at the level of 80% and conductivity above 1 $\mathrm{S\,cm^{-1}}$. Such level of transmittance is generally satisfied by TCO films, but known *p*-type TCOs like delafossites $CuAlO_2$, $CuGaO_2$, $SrCu_2O_2$ are characterized by conductivity below $1\ \mathrm{S\,cm^{-1}}$. *P*-type conduction of NiO as a main advantage in transparent conductive oxides is intrinsically formed on condition that the atomic ratio O/Ni exceeds 1. Nevertheless, above requirements should be ensured through the choice of fabrication method and optimization of process parameters for controlled NiO growth.

Thin NiO films are grown using many different chemical and physical methods. The more popular seem to be magnetron sputtering [8], evaporation [9, 10], sol–gel [11] or laser ablation deposition [12]. Here we present electrical and transparent properties of NiO films formed by radio frequency (RF) magnetron sputtering, as well as their thermal stability. Although some experimental studies on NiO film deposition at room and/or high temperature were published in last years [13, 14], crucial influence of growth temperature on semiconducting properties of NiO film was not strongly emphasized up to now. Moreover, the influence of carbon doping on transmittance and resistivity of NiO film is here also shown.

2. Experiment

Semiconducting NiO films were formed using unbalanced magnetron sputtering from a 3" NiO target in an O_2–Ar gas mixture at controlled temperatures from room temperature (RT) up to 700 °C. Quartz and *n*-Si(100) (resistivity of 1 Ωcm) samples were used as substrates at the distance of about 8 cm from the target. For deposition at elevated temperature the target was moved about 3 times farther from the hot substrates. The power of RF source was 150 W or 200 W. High purity of the film was accessible thanks to 4*N* purity of the target and 6*N* purity of the process gases, as well as a background pressure of 5×10^{-7} mbar. Doping of NiO by carbon was done by co-sputtering using C target supplied by a direct current (DC) source with power of 50 W. Total pressure during sputtering was maintained in the range of 5×10^{-3}–1×10^{-2} mbar. Transmittance of films was measured by Perkin–Elmer Lambda UV/VIS/IR spectrophotometer. Morphology of films was observed using scanning electron microscopy (SEM), the structure by X-ray diffraction and atomic composition was measured by electron dispersive X-ray spectroscopy. Electrical properties such as mobility μ and concentration of carriers were measured by the Hall method in the van der Pauw geometry, and resistivity ρ by the four point probe. Ohmic contacts (o.c.) to NiO films were sputtered gold pads in the corners of the square-shaped samples. Post-deposition annealing in oxygen or argon was applied to improve parameters of NiO films and to study their stability. For discussion of the results we introduce a factor ϕ_{O2} to represent a relative amount of oxygen in the sputtering gas mixture. It is defined by equation:

$$\phi_{O2} = \frac{f_{O2}}{f_{O2} + f_{Ar}}$$

where f_{O2} and f_{Ar} symbols signify oxygen and argon flows, respectively.

3. Results and discussion

3.1. Films deposited at room temperature

In terms of different transmittance levels we distinguish two types of NiO films. First type is one having transmission lower than 10% in the visible region. These are films deposited at room temperature in O_2–Ar plasma. Second group concerns films deposited at controlled temperatures elevated to 700 °C. For NiO films deposited at room temperature, we observed that increasing of oxygen partial pressure results in higher transmittance in the visible wavelength region and lower resistivity. Figure 1 shows transmittance of mentioned films. Band gap width values were extracted from absorption edge for every sample. We have assumed that the NiO films are characterized by a direct band gap as stated for the bulk NiO material. Extrapolation

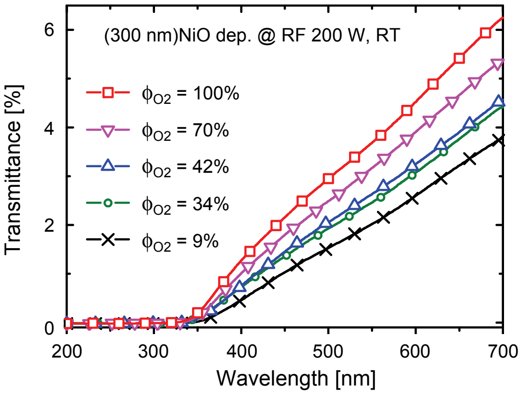

Fig. 1. Variation of transmittance of 300 nm NiO films deposited at room temperature versus oxygen amount ϕ_{O2} in gas mixture.

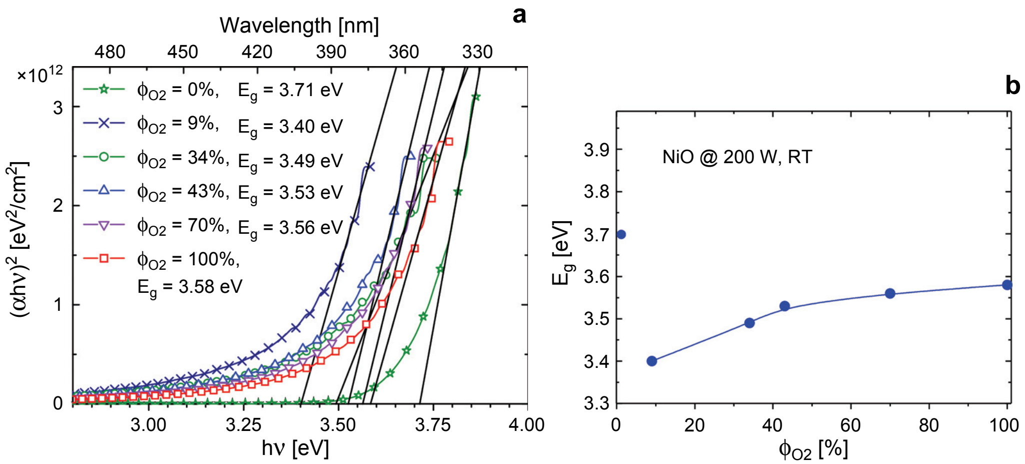

Fig. 2. Calculation of absorption edges (**a**) and dependence of band gap widths E_g on oxygen amount ϕ_{O2} for NiO films deposited at RT (**b**).

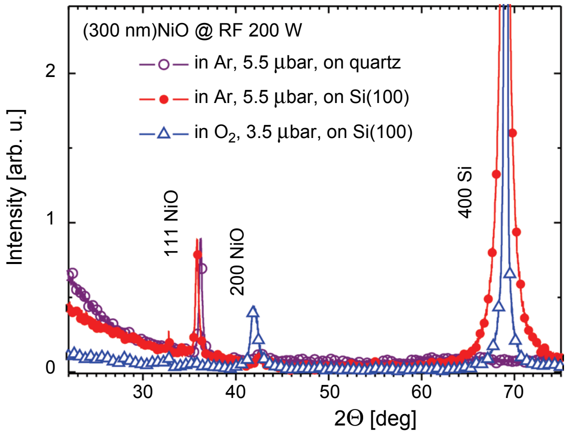

Fig. 3. XRD spectra of NiO films deposited at RF power of 200 W, room temperature, in O_2 or Ar ambient, on Si(100) or quartz substrate.

of linear part of square function of absorption coefficient $(\alpha h\nu)^2$ to zero gives band gap width, which is depicted in Fig. 2. If the relative amount of oxygen ϕ_{O2} is increased from 9% to 100%, then band gap width increases from 3.4 eV to 3.58 eV. The highest band gap width $E_g = 3.71$ eV is obtained for the film deposited at $\phi_{O2} = 0\%$. This exception can be connected with better crystalline quality of the NiO film observed by XRD as well as with lower density of intrinsic defects responsible for electrical conduction. The analysis of the structure of deposited NiO films reveals *fcc* structure of polycrystalline NiO grains with texture depending on oxygen content in plasma and on substrate temperature. XRD spectra of NiO films deposited at RT and RF power of 200 W are shown in Fig. 3. The NiO film deposited in oxygen onto Si(100) is composed of polycrystalline grains described by texture in ⟨200⟩ direction, of maximum size about 80 nm evaluated from SEM and lattice parameter of 4.286 Å calculated from 200 Bragg reflection. Such high lattice constant might be caused by incorporation of elevated number of oxygen atoms into the crystal, what correlates well with the lowest resistivity of 0.125 Ωcm at hole concentration of 2×10^{20} cm^{-3} attained for this film. The film deposited in argon plasma at RT is characterized by texture in ⟨200⟩ direction and lattice parameter of 4.28 Å or 4.276 Å for Si(100) or quartz substrate, respectively. Films deposited at low oxygen amount ϕ_{O2} in plasma and at RT are characterized by polycrystalline structure without texture and one phase of NiO.

As mentioned before for low transparent NiO films deposited at RT, increasing oxygen amount ϕ_{O2} causes film resistivity to decrease. It varies from 65 Ωcm for film deposited in pure argon ambient to 0.125 Ωcm for films deposited in pure oxygen. Composition of these well conductive NiO films was calculated from EDX spectra, and the analysis reveals atomic O/Ni ratio in the range of 1.1–1.2.

Annealing the NiO film in oxygen ambient at 300 °C for 30 min causes transmittance and band gap width to decrease slightly as is shown in Fig. 4. The mea-

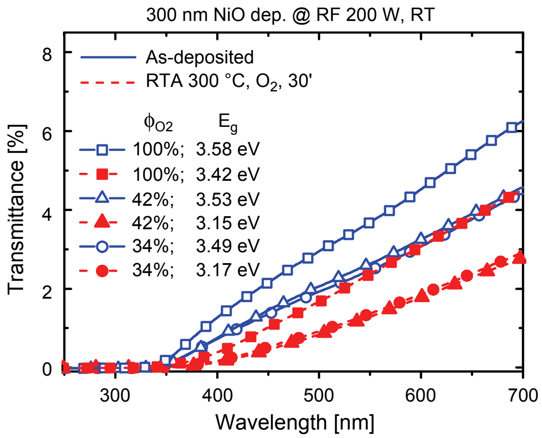

Fig. 4. Transmittance of NiO films as-deposited at RT, oxygen amount ϕ_{O2} and after annealing in O_2 at 300 °C for 30 min.

Table 1. Electrical parameters of NiO films deposited at RF power of 200 W, oxygen amount ϕ_{O2} and room temperature, as well as the parameters after annealing in oxygen at 300 °C for 30 min; p – hole concentration, μ – carrier mobility and ρ – resistivity.

		As-deposited			Annealed at 300 °C		
Sample	ϕ_{O2} [%]	p [1/cm^3]	μ [cm^2/Vs]	ρ [Ωcm]	p [1/cm^3]	μ [cm^2/Vs]	ρ [Ωcm]
NiO#10	9	5×10^{19}	0.2	0.36	1×10^{19}	2	0.3
NiO#3	34	1×10^{20}	0.15	0.18	7×10^{19}	0.2	1.6
NiO#6	100	2×10^{20}	0.36	0.12	3×10^{19}	0.5	2

surement results of electrical parameters for the films before and after annealing are presented in Tab. 1. The carrier concentration of annealed films decreases approximately one order of magnitude, but carrier mobility increases. Consequently, the resistivity becomes higher after annealing, apart from the film deposited at $\phi_{O2} = 9\%$. This may be explained by releasing oxygen from the NiO film. If NiO is deposited at oxygen content of 34% and above, the NiO films are characterized by high O/Ni ratio exceeding 1.18. What is important as well is the fact that annealing stabilizes electrical parameters of the samples. Hall measurements performed on deposited films give a mean percentage error of about 90% for carrier concentration, but after annealing the films new measurement results are less scattered and the error reaches about 60%.

3.2. Films deposited at high temperature

Thin NiO films deposited at elevated temperatures have much higher transmittance than those deposited at room temperature. The effect is shown in Fig. 5. The transmittance reaches 80% for films deposited at 500 °C. The resistivity of these films is higher than of those deposited at RT and some results are included in Tab. 2.

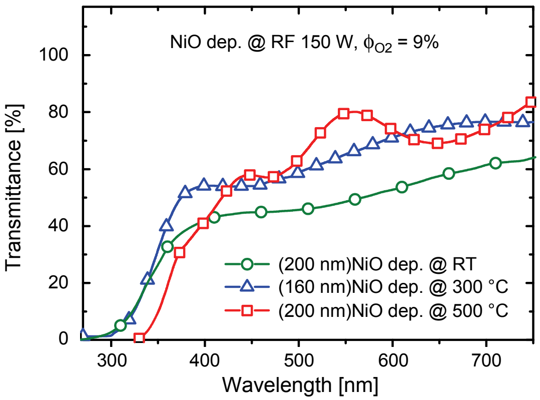

Fig. 5. Transmittance of NiO films deposited at oxygen content of 9%, at room temperature and elevated to 500 °C.

Table 2. Electrical parameters of NiO films deposited at elevated temperature T, RF power of 150 W and oxygen content ϕ_{O2}; p – hole concentration, μ – carrier mobility and ρ – resistivity.

Sample	T [°C]	ϕ_{O2} [%]	p [1/cm^3]	μ [cm^2/Vs]	ρ [Ωcm]
NiO#6	300	9	7×10^{14}	200	40
NiO#2	500	33	2×10^{17}	7.2	4.5
NiO#7	700	50	5×10^{16}	1.2	100

We observed that for the annealing to have a significant effect on thin NiO films it must be performed in temperature higher than the deposition process temperature. Optical properties of films deposited at 700 °C and then annealed in O_2 at 300 °C did not change in practice.

When the films deposited at elevated temperatures are annealed in oxygen at temperatures higher than process temperatures, resistivity increases strongly. The conductivity of the film deposited at 700 °C and next annealed at 900 °C is not measurable by applied techniques. The results of resistivity measurements before and after annealing are shown in Tab. 3. The sample marked in Tab. 3 as NiO#j3 is the NiO film doped with carbon, by co-sputtering at 500 °C. We discovered that incorporating a little amount of carbon into NiO results in lower film resistivity. The transmittance of the sample is 45% in the visible region. The band gap width is 3.89 eV, which

Table 3. Resistivity ρ of the NiO films deposited at elevated temperature T and after annealing in oxygen at temperature T_{ann} for 30 min.

Sample	Deposition parameters		ρ [Ωcm]	Annealed in O_2	
	ϕ_{O2} [%]	T [°C]	(as-deposited)	T_{ann} [°C]	ρ [Ωcm]
NiO#j6	9	300	40	550	4
NiO#j3	9	500	3.3	700	3300
NiO#j7	9	700	100	900	10000

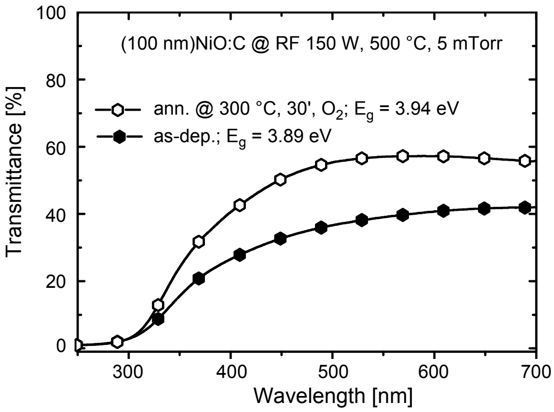

Fig. 6. Transmittance of 100 nm thick film of NiO doped with C by co-sputtering at $\phi_{O2} = 9\%$ and at supplied C target by DC power of 50 W, as well as the transmittance after annealing the sample in oxygen at temperature of 300 °C for 30 min.

is higher than of any undoped samples. Annealing at 300 °C in oxygen results in an increase in transmittance to a level close to 60% and an increase in band gap width to 3.94 eV, as shown in Fig. 6.

We observed that annealing NiO in argon at 250 °C or above results in a decrease in hole concentration and an increase in carrier mobility. As a consequence of 30 min annealing of NiO films their resistivity rapidly increases about 10 times or a few tens at higher annealing temperature. The transmittance of NiO films deposited at room temperature and $\phi_{O2} = 42\%$ changed from about 6% after deposition to about 60% after annealing in Ar at 600 °C for 30 minutes as it is shown in Fig. 7. The film resistivity increased 3 orders of magnitude. A similar optical effect in NiO films caused by annealing in Ar was reported by AZENS *et al.* [3] and called “bleaching” of the film.

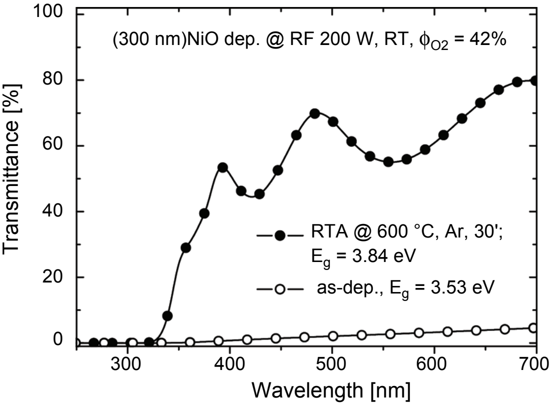

Fig. 7. Transmittance of (300 nm)NiO film deposited at RT, $\phi_{O2} = 42\%$ and power of 200 W, as well as after annealing the sample in Ar at temperature of 600 °C for 30 min.

3.3. Semiconducting properties of NiO

Research on conductivity of *p*-NiO films was performed in air at the temperature range from 20 °C to 250 °C. Resistivity was measured on a fabricated resistor with (300 nm)NiO film deposited in oxygen at RF power of 200 W and RT. Au ohmic contacts were formed on the ends of the resistor. Resistivity shown in Fig. 8 decreases with increasing temperature. The inset in the figure shows the dependence of conductivity (plotted on a logarithmic scale) versus the inverse temperature. This strongly suggests that the concentration of acceptors increases with temperature. The dependences are approximately linear in the temperature range of 30–110 °C, as well as in the higher range from 110 to 250 °C. Nevertheless some differences in activation energy E_a for native acceptor are observed: $E_a = 0.09$ eV in the lower temperature range and $E_a = 0.13$ eV in the higher range for the as-deposited NiO film. The measurement of the film annealed in O_2 at 300 °C for 30 min reveals the same activation energy in the lower temperature range, but $E_a = 0.10$ eV in the higher range. The differences in calculated E_a for the layer can be connected with conductivity through grain boundaries – the carrier scattering is less obvious at lower temperature energy, but the carrier scattering can be stronger at higher temperature. Moreover, the annealed film reveals a bit higher E_a at the second temperature range than the as-deposited film because of lower defect density in the NiO film, as we can suppose due to measured lower hole concentration and higher hole mobility in the film.

Similar thermal studies of NiO film conductivity presented in the paper [15] suggested the correlation between activation energy and average size of NiO grains. Described results concern NiO film formed by oxidation of Ni films, where activation energy of 0.085 eV was evaluated for the 300 nm thick NiO film. A small discrepancy in the results for activation energy E_a can be connected with the difference in crystal structure as well as in composition – high concentration of carbon (~20 at.%) existed in their films formed by oxidation, while the atomic concentration of carbon in our NiO films is observed below 1.5%.

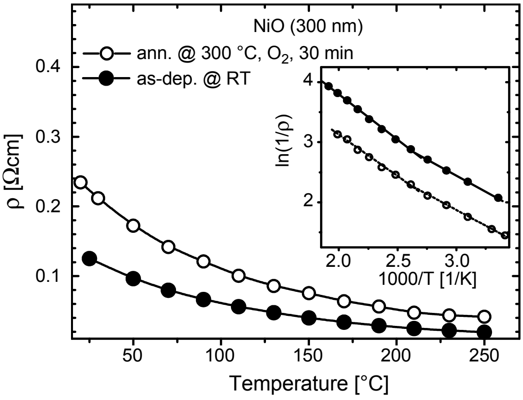

Fig. 8. NiO resistivity *ρ* vs. temperature for (300 nm)NiO film deposited at RF power of 200 W, RT in oxygen as well as after annealing the film at 300 °C in oxygen for 30 min. The inset – Arrhenius plot.

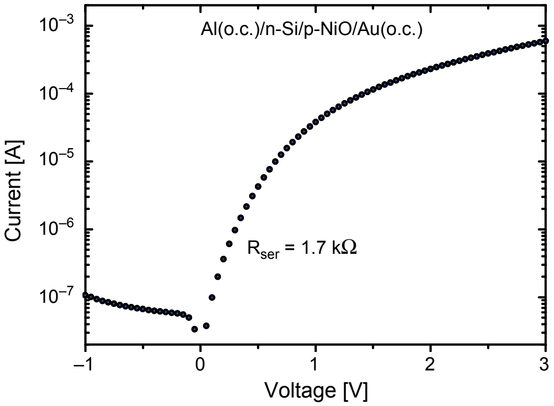

Fig. 9. Current–voltage characteristics of 0.3 mm diameter diode Al(o.c.)/*n*-Si/*p*-NiO/Au(o.c.). The NiO film deposited at RF power of 200 W, room temperature in oxygen; R_{ser} – series resistance.

The quality of semiconducting properties of *p*-NiO film was verified in *p–n* diode formed on *n*-Si. The ohmic contact with the Al film on the backside of Si sample was fabricated before NiO deposition, and (200 nm)Au film for ohmic contact to *p*-NiO was deposited onto NiO circles with 0.3 mm diameter using a lift-off technique. Current–voltage measurements confirmed good characteristics of *n*-Si/*p*-NiO junction diode shown in Fig. 9. The series resistance of 1.7 kΩ was calculated for an qualitative evaluation using a method described by CHEUNG *et al.* [16]. High series resistance is here observed because of high resistivity of the Si substrate.

4. Conclusions

Electrical parameters and optical transmittance of NiO thin films deposited at different temperature and O_2/Ar gas mixture during RF magnetron sputtering are presented. The properties of thin NiO films are strongly dependent on substrate temperature as well as on the amount of oxygen during sputtering. Relatively good transmittance and high resistivity is characteristic of the NiO films deposited at elevated temperature. The highest transmittance of about 80% at wavelength of 550 nm was observed for the NiO film deposited at the temperature of 500 °C and this film has resistivity of 110 Ωcm.

Very high conductivity *p*-NiO films reveal low transmittance, which is observed for films deposited at RT and the oxygen amount not less than 9%. Band gap width obtained for these films is in the range of 3.4–3.58 eV. The lowest resistivity of 0.125 Ωcm is measured for the film deposited at RT in pure O_2. *P*-type conductivity of this film measured from RT to 250 °C increases with temperature and the calculated from Arrhenius plot carrier activation energy is 0.09 eV at the temperature up to 110 °C.

Noticed correlation of high transmittance with low conduction is strong. The effect of bleaching observed on high conductive NiO film after annealing in argon at 600 °C is associated with a sudden rise in film resistivity. The NiO films deposited at 500 °C are characterized by transmittance in the visible range close to 80%, hole concentration in the level of 10^{17} cm^{-3}, mobility of 7 $\mathrm{cm}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$ and resistivity of few Ωcm.

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