Capability of Semiconducting NiO Films in Gamma Radiation Dosimetry

M. Guziewicz[a], W. Jung[a], J. Grochowski[a], M. Borysiewicz[a], K. Golaszewska[a],

R. Kruszka[a], A. Baranska[a], A. Piotrowska[a], B.S. Witkowski[b], J.Z. Domagala[a,b],

M. Gryzinski[c], K. Tyminska[c] and A. Stonert[d]

[a]Institute of Electron Technology, al. Lotników 32/46, 02-668 Warsaw, Poland

[b]Institute of Physics, Polish Academy of Sciences, al. Lotników 32/46, 02-668 Warsaw, Poland

[c]Institute of Atomic Energy, 05-400 Otwock-Świerk, Poland

[d]The Andrzej Sołtan Institute for Nuclear Studies, Hoża 69, 00-681 Warsaw, Poland

Electrical properties of RF magnetron sputtered p-NiO films were characterized after fabrication and after gamma irradiations using ^{137}Cs and ^{60}Co sources. Electrical parameters are obtained from the Hall measurements, impedance spectroscopy and C–V measurement of n-Si/p-NiO junction diodes. The results show that resistivity of the NiO film is gradually increased following after sequential irradiation processes because of the decrease in holes' concentration. Hole concentration of a NiO film decreases from the original value of 4.36×10^{16} cm^{-3} to 2.86×10^{16} cm^{-3} after ^{137}Cs γ irradiation with doses of 10 Gy. In the case of γ irradiation from ^{60}Co source, hole concentration of the film decreases from 6.3×10^{16}/cm^3 to 4.1×10^{16}/cm^3 and to 2.9×10^{16}/cm^3 after successive expositions with a dose of 20 Gy.

PACS: 73.61.Jc, 29.40.–n, 87.53.Bn

1. Introduction

Nickel oxide is an interesting material due to its semi-transparent, semiconducting, thermoelectric and catalytic properties [1–3]. It is characterized by a direct band gap of about 4 eV and a possible wide range of resistivity dependent on the growth method. Some of potential applications of NiO films in electronic devices like gas sensors, counter electrodes, displays, LEDs or variable reflectance mirrors require well controlled electrical parameters. Moreover, NiO films were considered to serve as a reliable passive gamma detector, especially for application in clinical dosimetry. Some optimistic results were previously demonstrated in the papers [4, 5], but observed changes in the current–voltage characteristics were not clarified. To verify this application possibility some test structures like NiO film resistors and heterojunction diodes n-Si/p-NiO were fabricated and next exposed to gamma radiation to disclose capability of this semiconductor in gamma sensor applications. The measurements of NiO properties concern film resistivity, hole concentration, mobility as well as impedance of the p–n diode structures. Possible changes in NiO films during gamma exposition can be justified by numbers of possible collisions of γ photons with atoms. An explanation is proposed using spectra of the absorbed energy in the film. The spectra are calculated by means of the Monte Carlo simulations.

2. Experimental

Thin films were deposited by RF unbalanced magnetron sputtering from 3″ NiO target (99.99% purity) in O_2/Ar plasma (99.9999% purity gases) onto n-Si(001) and quartz substrates at room temperature (RT), power

P_{RF} of 200 W. Oxygen content F_{O2} in the plasma is defined by pressures ratio of $p_{O2}/(p_{O2} + p_{Ar})$, where p_{O2} is partial oxygen pressure, p_{Ar} is argon pressure. Morphology and structural properties of the films were characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The compositions of the films were estimated by energy dispersive analysis of X-rays (EDAX) and compared with the Rutherford backscattering spectrometry (RBS) method. Electrical parameters were obtained from the Hall measurements in van der Pauw geometry and capacitance–voltage (C–V) measurements of n-Si/p-NiO junction.

As a n-type Si substrate for fabrication of n–p junction were used high conductive samples cut from a 4″ Si(001) wafer with resistivity of 0.005 Ω cm and with 5 μm thick epitaxial layer doped to $n = 8 \times 10^{15}$ cm^{-3}. The Si samples were metallized by sputtering of (200 nm) Ti film on the backside and next annealed in Ar at 600 °C for 5 min to form Ti-silicides ohmic contact. Such prepared substrates were deoxidized in buffered hydrofluoric acid before NiO deposition. A pattern of circles with 1 mm diameter was applied during photolithography to fabricate n-Si/p-NiO junction diodes with 300 nm or 400 nm thick NiO film sputtered at room temperature. (200 nm) Au top contact layer was deposited by sputtering and *lift off* technique to form ohmic contact to the NiO films. The samples were sealed from air by deposition of (150 nm) SiO_2 film using plasma enhanced chemical vapor deposition (PECVD) at temperature of 300 °C.

The test structures were exposed to γ radiation using ^{137}Ce source of 660 keV energy photons and ^{60}Co source of 1332 keV photons. The structures were characterized using capacitance–voltage (C–V) and impedance meth-

ods. *C–V* characteristic is taken at frequency of 10 kHz, impedance is measured at frequency range from 0.5 kHz to 2 MHz and results are presented in form of the Nyquist plots.

Some theoretical calculations of absorbed energy by thin film NiO lying on Si substrate during gamma irradiation were performed using the general Monte Carlo *N*-particle transport code (MCNP) Ver. 5 developed at Los Alamos National Laboratory. The code dedicated to compute neutron, photon, electron, or coupled neutron/photon/electron transport in materials is here used to calculate interactions of high energetic photons and electrons with materials. The code accounts incoherent scattering, photoelectric absorption, absorption in pair production with local emission of annihilation radiation, and *bremsstrahlung*. The material is defined by atomic composition of elements and mass density. Densities of typical NiO crystal (6.72 g cm^{-3}) and Si crystal (2.329 g cm^{-3}) have been applied here. The sample is stroked by 662 keV or 1332 keV photons emitted by a point source displaced from the sample for a distance of 3.5 m.

3. Results and discussion

3.1. NiO film properties

Conductivity of single crystal stoichiometric NiO is commonly very low, but for NiO in form of polycrystalline film, when formation of point defects is more probable, conductivity is well measurable. Applied sputtering method allowed to produce non-stoichiometric nickel oxide due to controlled oxygen flow into the O$_2$–Ar plasma. We observed that an increase in oxygen content in gas mixture results in decrease of film resistivity and this can be explained by increase of holes' concentration as shown in Fig. 1. This result is concurrent with the ones obtained by Hotový et al. [6]. In the case of sputtering only in Ar, the film resistance is sometimes extremely high — sheet resistance of about 4 GΩ/sq is observed for the NiO film deposited at 150 W. High resistivity of the NiO films is associated with low hole mobility in the range of 0.02–0.8 cm^2/(V s). For sputtering in oxygen, holes' concentration reaches the level of 10^{20} cm^{-3} and resistivity goes to the minimum of 0.14 Ω cm. These results are consistent with the model of *p*-type conduction in NiO for atomic composition at ratio O/Ni exceeding 1 and confirmed by EDX measurements of the ratio to be 1.1 < O/Ni < 1.26 for our *p*-type films. Comparative study of the composition on few NiO samples by 2 MeV He$^+$ RBS measurement confirmed the range within an error of ±0.02 connected with evaluation of presence of residual carbon.

XRD study of deposited NiO films revealed fcc structure of polycrystalline grains with texture dependent on oxygen content in plasma and temperature — ⟨111⟩ texture for deposition in Ar and ⟨200⟩ texture for deposition in O$_2$ [8]. The sizes of grains are in the range 20÷50 nm. Calculation of NiO lattice parameter revealed lattice constant increased from 4.194 Å to 4.303 Å for films deposited at oxygen content in gas mixture from 9% to 50%,
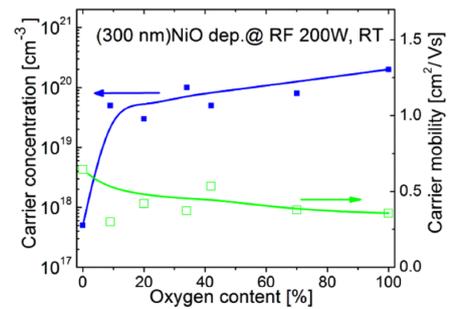

Fig. 1. Influence of the oxygen content in the gas mixture on the concentration and mobility of carriers of a 300 nm thick NiO film. The film deposited at 0% O$_2$ content exhibited *n*-type conductivity with resultant electron concentration at a level of 5×10^{17} cm^{-1} (±80%).

respectively. These values are larger than the lattice constant of 4.177 Å characterizing bulk material. It should be mentioned that after annealing the films at 300 °C or above, the constant is decreased.

3.2. Influence of γ radiation on NiO electrical properties

Study on electrical properties of *p*-NiO film after γ irradiations was performed by using both *C–V* and impedance measurements of the *p–n* diodes. The diode with *p*-NiO deposited at 20% oxygen content is characterized by diffusion potential 0.64 V and rectifying current ratio $I_{\mathrm{ON}}/I_{\mathrm{OFF}}$ of ≈ 10^3. The *C–V* measurement allows to calculate carrier concentration of *p*-NiO based on carriers interactions at *p–n* heterojunction. The calculation is given by Eq. (1) [7]:

$$N_{\mathrm{a}} = n_{\mathrm{Si}} N^* / (n_{\mathrm{Si}} - N^*), \tag{1}$$

where N_{a} — acceptor concentration in NiO, N^* is resultant concentration of carriers near the junction interface calculated from the Mott plot obtained from *C–V* measurements, n_{Si} — electron concentration in Si. The resultant carrier concentration was measured as $N^* = 7.1 \times 10^{16}$ cm^{-3} and the acceptor concentration was calculated to be $N_{\mathrm{a}} = 6.3 \times 10^{16}$ cm^{-3}. Such low value of acceptor concentration is caused partially by processes of photolithography and metallization to NiO, but most likely it is a result of potential barriers on NiO grain boundaries and of existing traps. In a consequence we observe decrease in hole concentration measured by the *C–V* method in this case.

The diode was exposed twice by 1332 keV γ source to a dose of 20 Gy each time. As an example, a resultant carrier concentration of N^* of the diode after irradiations is shown in Fig. 2. The resultant carrier concentration was decreased from original 7.1×10^{16} cm^{-3} to 6.7×10^{16} cm^{-3} and to 6.28×10^{16} cm^{-3} for the diode irradiated for the first and second time, respectively. The hole concentration in NiO film was calculated to be 4.12×10^{16} cm^{-3} and 2.9×10^{16} cm^{-3} after the first and second irradiation, respectively. Impedance of the diode measured at
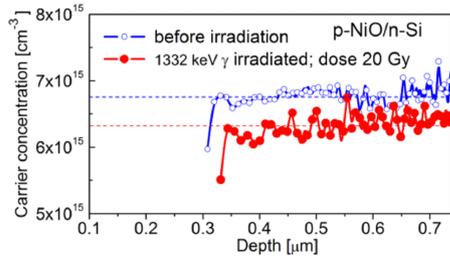
Fig. 2. The resultant carrier concentration N^* measured at the p-NiO/n-Si junction vs. the junction depth calculated from the C–V plots for the diode before and after γ irradiation using ^{137}Ce source.

frequency from 0.5 kHz to 2 MHz is presented in the form of the Nyquist plots in Fig. 3. The impedance functions $Z(\omega) = R(\omega) - \mathrm{i}X(\omega)$ are visible here as two semicircles, where this on the right side is registered at lower frequency and it is related to the junction diffusion capacitance. Symbols represent experimental data while continuous lines are simulated. The simulations involved a model for the forward bias conditions consisting of three RC impedance circuits in a series taken with the series resistance R_s. Seven parameters were here engaged in the calculations and the results are shown in Fig. 3b and c. Parameters C_1 and C_2 are correlated with diffusion capacitance, C_3 is associated with space charge capacitance, R_1, R_2 and R_3 are parallel resistances related to the NiO film and R_s is a series resistance. Calculated resistances of NiO film R_2 and R_3 are significantly increased about few times after the γ irradiation, while capacitances of C_1, C_2, and C_3 remain on similar level.
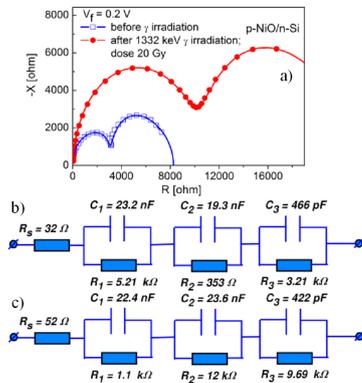

Fig. 3. (a) Nyquist plots measured at frequency from 0.5 kHz to 2 MHz on p-NiO/n-Si diode 1332 keV γ irradiated ones and second time with dose of 20 Gy. A model of RC circuits for the samples before (b) and after (c) the last irradiation using ^{60}Co source.

A similar diode with NiO film having originally concentration $p = 4.9 \times 10^{16}$ cm^{-3} was exposed to the ^{137}Cs γ irradiation with a dose of 18 Gy and characterized using similar techniques. C–V measurements resulted in concentration $N_\mathrm{a} = 3.2 \times 10^{16}$ cm^{-3} for the NiO film reveal-

ing strong effect of the dose on decreasing carriers concentration. Nyquist plots from the impedance measurements are presented in Fig. 4a and following simulated results are shown in Fig. 4b and c. The series resistance increased about 30 times while diffusion capacitance decreased about 16 times after exposition. Resistance of the NiO film is higher by one order of magnitude, while space charge capacitance has been reduced as results of the γ exposition to dose of 18 Gy.
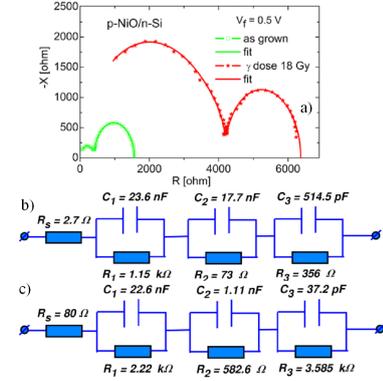

Fig. 4. (a) Nyquist plots measured at frequency from 0.5 kHz to 2 MHz on p-NiO/n-Si diode before and after 662 keV γ irradiation with dose of 18 Gy using ^{137}Ce source. A model of RC circuits for the samples before (b) and after (c) the irradiation.

This is consistent with the measurement of the Hall structures with a corresponding NiO film, suggesting a reduction in both concentration and mobility of holes in the film after ^{137}Cs γ irradiations. The results are roughly concurrent with measurements of NiO resistivity using NiO film resistors. The resistance increases successively $0.5 \div 1.5\%$ with increase in irradiation dose of 1 Gy. When the p–n diode is irradiated sequentially with dose of 2 Gy every times, we observe that hole concentrations of a NiO film decreases from the original value of 4.36×10^{16} cm^{-3} to 2.86×10^{16} cm^{-3} after five such irradiations yielding total dose of 10 Gy.

Our study shows that the effect of the γ irradiation with 1332 keV photons on hole concentration is stronger than the effect of 662 keV γ irradiation at a similar dose. This higher decrease in hole concentration seems to be consistent with increased probability of multiple interactions as well as probability of electron–positron pairs creation due to sufficiently high energy.

3.3. MC simulation of γ absorption by NiO film

The mechanism responsible for observed change in electrical parameters of the NiO film that we propose assumes damaging Ni–O bonds, which in turn causes destruction of Ni^{3+} ions responsible for hole conduction. This process lowers the number of holes and therefore changes the electrical characteristics of the NiO films. A basic question is if highly energetic photons are able to hinder stability of the bonds in the thin NiO film. In

order to answer the question, the MC simulations of interaction of 662 keV photon with the $(0.6\ \mu\text{m})$NiO film were performed for the sample $(0.6\ \mu\text{m})$NiO/$(0.5$ mm) Si located in air or vacuum, as well as for the $(6\ \mu\text{m})$NiO/$(0.5$ mm) Si in vacuum. As a result of simulations we get the pulse height tally which provides the energy distribution of pulses created in a cell that models a physical detector.
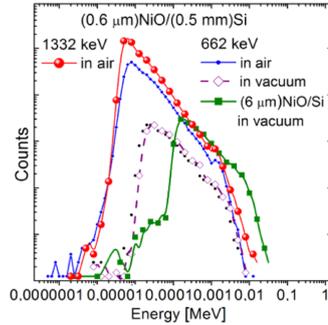

Fig. 5. Spectrum of energy absorbed in the NiO film for a MCNP detector model of $(0.6\ \mu\text{m})$NiO/$(0.5$ mm) Si displaced from the γ source in air or in vacuum, as well as for a detector model of $(6\ \mu\text{m})$NiO/$(0.5$ mm) Si in vacuum. Spectrum is normalized to the one photon emitted by a point source of the 662 keV or 1332 keV photons.

The spectrum shown in Fig. 5 provides information about the energy absorbed in the NiO film. Spectrum is normalized to the one photon emitted by a point source of the 662 keV or 1332 keV photons. A very low counts level of 10^{-7} was recorded for the film situated in vacuum (not shown here), but the film placed in air is able to absorb energy strongly — even higher by a few orders of magnitude. Increased absorption in the NiO film is due to secondary effects of photon interactions with Si substrates as well as scattering processes in air, where high energy electrons are created and these strike the NiO film. The interaction processes influencing the NiO absorption cover an energy range from 0.3 eV to 10 keV and reveal local maxima. Other simulations for the case of 6 μm thick NiO film on the Si substrate show that the absorption range is increased to 30 keV and the position of the maximum is moved to 200 eV. In the case of MC simulations of interaction of 1332 keV photon with the $(0.6\ \mu\text{m})$NiO film on the $(0.5$ mm) Si sample located in air, it reveals a wider energy range of the spectra as well as maximum peak of the spectra is on the level about 3 times higher than the spectra for the 663 keV photon. The effect is also due to electron–positron pairs creation possible at this level of photons energy. The higher possibility of interaction with 1332 keV photon and its' absorption in the NiO film can explain stronger influence of the irradiation on decrease in hole concentration.

Although the MCNP V.5 does not allow an identification of the damaged Ni–O bonds or defects created in the crystal, the spectra reveal extensive numbers of diverse energetic states which are absorbed in the thin film, some of which can cause significant damage to the band gap. In order to understand the mechanisms of radiation damages in wide band gap materials, new, more advanced models have to be designed and implemented.

4. Conclusions

The test diodes p-NiO/n-Si were exposed to γ sources and characterized using C–V and impedance methods. Measurement of the diode after irradiation with 662 keV photons for a low dose of 2 Gy showed increases in real and imaginary parts of the NiO impedance. This can be explained by the decrease in hole concentration. This was proved by C–V measurements of the p–n junction, which showed reduced hole concentration in the NiO film. Moreover, it was observed that NiO resistivity is increased after subsequent higher dose γ irradiations. Increase in dose to 10 Gy results in stronger decrease in hole concentration from the original value of 4.9×10^{16} cm^{-3} to 3.26×10^{16} cm^{-3} after ^{137}Cs γ irradiation with doses of 18 Gy. The effect of irradiation to similar dose (20 Gy) using 1332 keV photons from ^{60}Co source is stronger, as hole concentration is decreased from 6.3×10^{16} cm^{-3} to 2.9×10^{16} cm^{-3}. The changes are qualitatively justified by the Monte Carlo simulations of absorbed energy by NiO film exposed to gamma radiation from ^{137}Cs and ^{60}Co sources.

Experimental results show strong influence of γ irradiation dose on decrease in hole concentration of NiO and increase in real and imaginary parts of impedance of the p–n diode. On the other hand increase in film resistivity observed on γ irradiated film resistors at direct current is less pronounced. A possible application of NiO film as passive dosimeter requires additional optimization of film thickness, geometry of the structure as well as measurement conditions to extract better sensitivity of measured resistivity on dose unit.

References

[1] G.A. Sawatzky, J.W. Allen, *Phys. Rev. Lett.* **53**, 2339 (1984).

[2] Z. Ying, G. Donghong, G. Yongyou, G. Fuxi, *Mater. Sci. Eng B* **135**, 125 (2006).

[3] W. Shin, N. Murayama, *Mater. Let.* **45**, 302 (2000).

[4] K. Arshak, O. Korostynska, F. Fahim, *Sensors* **3**, 176 (2003).

[5] K. Arshak, O. Korostynska, D. Morris, *Mater. Sci. Eng. B* **118**, 275 (2001).

[6] I. Hotový, J. Huran, J. Janík, A.P. Kobzev, *Vacuum* **51**, 157 (1998).

[7] M. Guziewicz, J. Grochowski, M. Borysiewicz, E. Kaminska, J. Domagała, W. Rzodkiewicz, K. Gołaszewska, B. Witkowski, R. Kruszka, M. Ekielski, A. Piotrowska, *Opt. Appl.* **41**, 431 (2011).

[8] S.O. Kasap, *Principles of Electronic Materials and Devices*, McGraw-Hill, New York 2002.