PHYSICAL MECHANISMS OF ENHANCED CONDUCTIVITY IN IRRADIATED InO_x NANOCRYSTALLINE FILMS

M. Bender[1], N. Katsarakis[1], G. Kiriakidis[1], I.A. Ovid'ko[2] and A.B. Reizis[2]

[1] Photonic and Electronic Materials Laboratory, Materials Science Group, Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas PO Box 1527, Vasilika Vouton, 711 10 Heraklion, Crete, Greece

[2] Institute of Problems of Mechanical Engineering, Russian Academy of Sciences, Bolshoj 61, Vasil. Ostrov, St. Petersburg, 199178, Russia

Abstract. We present experimental data on the conductivity evolution in InO_x nanocrystalline (nano-grained) films after UV light irradiation, and its dependence on film thickness. These experimental data are indicative of new irradiation-induced effects in the nanocrystalline matter and used as input in elaboration of a theoretical model describing physical mechanisms of the UV light irradiation-induced enhancement of the conductivity in nanocrystalline films. In the framework of the model, the experimentally detected peculiarities of InO_x nanocrystalline films are attributed to the presence of high-density ensembles of grain boundaries in such films. In particular, the enhancement of conductivity in these films is theoretically described as a phenomenon related to irradiation-induced structural transformations of grain boundaries and ionization, whose intensities are highly sensitive to the film thickness.

Nanocrystalline films recently have attracted a tremendous attention due to their outstanding properties associated with nanoscale and interface effects; see, e.g., [1-3]. In particular, indium oxide (InO_x) nanocrystalline films have exhibited remarkable ozone sensing properties at room temperature after UV light irradiation [4-8]. Such films change their conductivity more than five orders of magnitude after photoreduction with UV light exposure and subsequent oxidation in ozone atmosphere in a fully reversible manner. In doing so, it has been experimentally revealed that the ozone sensing properties of InO_x nanocrystalline films essentially depend on many factors such as film thickness, ozone concentration, grain size, etc. [4-8]. It is indicative of a complicated nature of the ozone sensing of nanocrystalline InO_x films, whose micromechanisms have been not yet experimentally identified and/or theoretically described in the unambiguous way. The main aims of this work are to report new experimental data on the conductivity evolution of InO_x nanocrystalline films after UV light irradiation and

its dependence on the film thickness as well to suggest a theoretical model which describes the UV light irradiation-induced effects in such films, with emphasis on the specific detected features exhibited by the irradiated nanocrystalline matter.

On the experimental side, the depositions of the InO_x nanocrystalline films of various thickness H values were carried out by DC magnetron sputtering in an Alcatel sputtering system with a 99.999% pure metallic indium target (15 cm diameter) at a pressure of $8 \cdot 10^{-3}$ mbar. The base pressure of the vacuum chamber was $5 \cdot 10^{-7}$ mbar. The InO_x films were deposited onto Corning 7059 glass substrates, which had thermally evaporated NiCr electrodes for conductivity measurements. All samples produced for this work were sputtered in pure oxygen atmosphere. The film thickness was varied from 10 to 880 nm. All other parameters, i.e. total pressure, composition of the sputtering atmosphere, and sputtering rate, were kept constant for all the depositions discussed here. The film thickness was measured by single-wavelength ellipsometry under different angles and

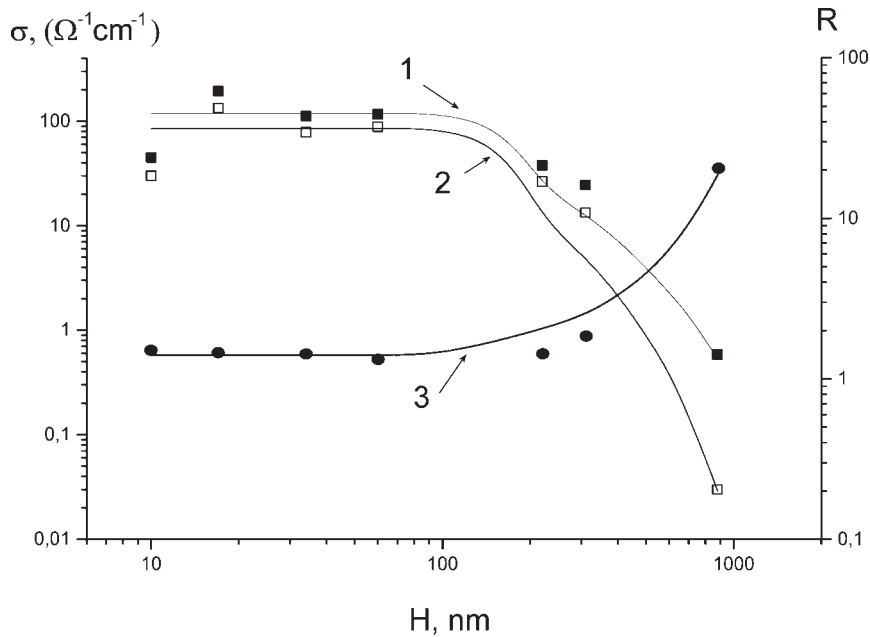Corresponding author: I.A.Ovid'ko, e-mail: ovidko@def.ipme.ru

Fig. 1. Experimentally measured values of σ_{max} (full boxes), σ_{min} (open boxes) and $R = \sigma_{max}/\sigma_{min}$ (full circles) in InO_x nanocrystalline films with various values of the thickness H. Theoretical dependences of σ_{max}, σ_{min} and R on the film thickness H are shown as curves 1, 2 and 3, respectively.

for the thicker films it was additionally estimated using a Talystep profilometer. The crystal structure of the films was determined by X-ray diffraction (XRD) using Cu Kα X-rays. All films but the thinnest ones with 10 nm and 17 nm thickness were found to be nanocrystalline with random orientation. The electrical characterization was performed in a specially designed reactor. For photoreduction the samples were directly irradiated in vacuum by the UV light of a mercury pencil lamp for 20 minutes in order to achieve a steady state. Consequently the UV lamp was switched off and the sample was kept in vacuum for two hours. An electric field of approximately 1 V/cm was applied to the samples and the electrical current was measured with an electrometer. In this work, all conductivity measurements were carried out at room temperature. The photoreduction treatment results in an increase of the conductivity of the InO_x films from a minimal value of 0.0001 $Ohm^{-1}\cdot cm^{-1}$ in its as grown insulating stage to the level of 0.5 to 200 $Ohm^{-1}\cdot cm^{-1}$ depending on film thickness. Subsequently, films exhibited a conductivity decay in vacuum dropping to the corresponding levels of 0.03 to 130 $Ohm^{-1}cm^{-1}$ after two hours. This behavior was completely reversible through many cycles. In the following discussion, maximum conductivity denotes the conductivity in the conducting state of the sample after the irradiation procedure, while minimum conductivity denotes the conductivity after decay in vacuum for two hours.

The experimentally measured dependences of conductivities, σ_{max} and σ_{min}, and ratio $R = \sigma_{max}/\sigma_{min}$ on the films thickness H are presented in Fig. 1. σ_{max} is tentatively constant for H ranging from 10 to 100 nm and decreases with rising H, for $H > 100$ nm. The same character is inherent to $\sigma_{min}(H)$ which, however, decreases more abruptly in the range of H from 100 to 900 nm. As a result, R remains almost constant (~ 1.5) for H ranging from 10 to 100 nm while it was found to rapidly increase with rising H, for $H > 100$ nm.

Now let us turn to a theoretical analysis of evolution of the conductivity in UV irradiated InO_x nanocrystalline film, taking into account the experimental data reported (Fig. 1). It should be noted that, as with nanocrystalline InO_x films [4-8], amorphous InO_x changes its conductivity more than five orders of magnitude after UV light irradiation and subsequent oxidation in ozone atmosphere in a fully reversible manner [9]. In these circumstances, the phenomenon discussed can be naturally attributed to the specific structural peculiarities inherent to both amorphous and nanocrystalline solids. We believe these structural peculiarities to be a low atomic density (compared to that of the bulk crystalline phase) and disorder which characterize both the grain boundary phase in nanocrystalline solids fabricated at highly non-equilibrium conditions and the amorphous phase. (Sometimes, grain boundaries in nano- and polycrystalline materials have the amorphous structure (see experimental data [10-13] and mod-

els [14-17]), in which case the behavior of such amorphous grain boundaries is, in fact, identical to that of the "true" amorphous phase.) Below we will suggest a theoretical explanation of the experimental data presented in Fig. 1, based on the idea on the specific role of grain boundaries in irradiated nanocrystalline films. In doing so, we assume that the UV along with laser and other irradiation sources are responsible for the following two basic effects in nanocrystalline films:

(i) *Ionization.* High energy (UV) photons excite electrons in the valence band and transfer them into conductivity band, in which case the density n_e of carriers of electric current increases. The characteristic energy of such ionization (E_i) is in the order of 5 eV [18].

(ii) *Structural transformations of grain boundaries.* High energy (UV) photons induce the re-arrangements of atoms in the grain boundary phase, including transfer of atoms from grain boundaries (where vacancies are formed) to grain interiors. Since the atomic density of grain boundaries is lower than that of the bulk phase, atoms at grain boundaries can be re-arranged more easily than in the bulk phase. In this situation, the characteristic energy E_t of the process (ii) obeys the following inequality: $E_i < E_t < E_p$. Here E_p (~ 50 eV [18]) is the energy characteristic for the formation of interstitial atom/vacancy pairs in nanograin interiors. (This formation is assumed to be negligible in nanocrystalline films under UV light exposion, because of comparatively high value of its characteristic energy E_p.).

Process (i) gives rise to an abrupt increase of the density n_e of electrons that carry the electric current. However, excited electrons fastly move in the solid and are fastly trapped by ionized atoms, in which case the UV-irradiation-induced ionization effects disappear during a rather short relaxation time interval t_i after exposure.

On the other hand, grain boundaries are characterized by a low atomic density compared to the bulk or, in other terms, by the excess free volume [19,20]. In addition, atoms in the grain boundary phase are arranged more disorderedly than those in the bulk crystalline phase. In these circumstances, the characteristic energy E_t of UV-irradiation-induced re-arrangements of atoms at grain boundaries ranges rather widely with many re-arrangement acts (elemental structural transformations) having a characteristic energy E_t essentially lower than the characteristic energy E_p (~ 50 eV) of irradiation-induced formation of interstitial atom-va-

cancy pairs in the bulk phase. As a corollary, the process (ii) accompanied by ionization is capable of essentially contributing to the conductivity enhancement in InO$_x$ nanocrystalline films under UV irradiation.

In general, grain boundaries in semiconductors trap an excess number of majority carriers – either electrons or holes depending on whether the semiconductor is doped n- or p-type, respectively [19]. In doing so, grain boundaries are characterized by an excess electric charge Q_{gb} screened by a corresponding excess electric charge -Q_{gb} of the so-called compensating depletion layers on either side of the grain boundary. Electric-charge inhomogeneities associated with a grain boundary decrease conductivity, because the charge trapped at the boundary controls the barrier height and hence the current flow across the boundary [19]. (The same effect can be responsible for a dramatic suppression of the critical current density in polycrystalline high-T_c superconductors [21-23].) The electric-charge inhomogeneities associated with grain boundaries are characterized by some energy E_{el} and are sensitive to atomic arrangement in grain boundaries. In these circumstances, UV-irradiation-induced structural transformations leading to a release of the energy E_{el} are facilitated, while those leading to an increase of the energy E_{el} are hampered. The UV-irradiation-induced structural transformations of grain boundaries, that give rise to smoothing of electric-charge inhomogeneities and, therefore, to conductivity enhancement are facilitated, because the smoothing is accompanied by a release of E_{el}. This effect is of particular importance in the namely nanocrystalline materials where the volume fraction of the grain boundary phase is extremely high.

The reverse structural transformations of grain boundaries occur during some relaxation time interval t_t. This interval is much larger than t_i, the relaxation time interval for ionization induced by UV irradiation. In these circumstances, the experimentally detected [4-8] abrupt decrease of conductivity following the photoreduction and oxidation process in the ozone atmosphere can be naturally attributed to ozone diffusion along grain boundaries. Such grain boundary diffusion processes both facilitate the reverse structural transformations and give rise to trapping of electrons that carry electric current (because oxygen atoms serve as trapping centers for moving electrons). As a corollary, t_t decreases in the presence of an ozone atmosphere in more pronounced manner (up to five orders of magnitude) compared with the relaxation induced room temperature decay time t_t in vacuum discussed here.

Now let us discuss the dependence of conductivity parameters on the film thickness H in the case of UV irradiated InO nanocrystalline films. Experimental data ($\sigma_{max}(H)$ and $\sigma_{min}(H)$ dependences) presented in Fig. 1 can be qualitatively explained as follows, using the suggested representations on the UV light effects on the conductivity of nanocrystalline films. The UV photons that have enough energy to cause transformations of grain boundaries (ionization, respectively) in a nanocrystalline film are characterized by a penetration depth H_t (H_i, respectively). If H_t, $H_i < H$, intensities of UV irradiation-induced structural transformations of grain boundaries and ionization decrease dramatically with rising the film thickness H. In the first approximation we assume that the H-dependence of the intensity induced by transformations and ionization can be described respectively by the factors $\exp(-H/H_t)$ and $\exp(-H/H_i)$ (where $H_t < H_i$, because $E_t > E_i$.) In this situation, the conductivity of as-irradiated InO$_x$ nanocrystalline film can be approximately written as:

$$\sigma_{max} \approx \sigma_t \exp\left[-\frac{H}{H_t}\right] + \sigma_i \exp\left[-\frac{H}{H_i}\right]. \qquad (1)$$

Here σ_t denotes the conductivity enhanced by structural transformations of grain boundaries, and σ_i the conductivity enhanced by ionization processes near the film free surface.

Following our previous qualitative analysis, after decay in vacuum for time interval $t = 120$ min, ionization effects disappear, while the effects associated with structural transformations of grain boundaries do not. That is, σ_i abruptly decreases during a short relaxation time interval and does not contribute to σ_{min}. In these circumstances, the conductivity characteristics, σ_{min} and R, are approximately given by the following formulae:

$$\sigma_{min} \approx \sigma_t \exp\left[-\frac{H}{H_t}\right], \qquad (2)$$

$$R \approx 1 + \frac{\sigma_i}{\sigma_t} \exp\left[H\left[\frac{1}{H_t} - \frac{1}{H_i}\right]\right]. \qquad (3)$$

Formulae (1)-(3), for $H_t = 110$ nm, $H_i = 210$ nm and $\sigma_i/\sigma_t \approx 0.4$, describe in a semi-quantitative manner the experimentally detected tendencies of the dependences $\sigma_{max}(H)$, $\sigma_{min}(H)$ and $R(H)$; see theoretical dependences (curves 1, 2 and 3) in Fig. 1.

To summarize, in this work we have reported new experimental data on the effects of film thickness H on room temperature conductivity in InO$_x$ nanocrystalline films after UV light irradiation and its evolution in time. The experimentally measured H-dependences of conductivity σ_{max} and σ_{min} in as-irradiated films and after decay for 120 min time interval, respectively, and ratio $R = \sigma_{max}/\sigma_{min}$ are indicative of the new UV-light-induced effects and relaxation processes in nanocrystalline films. To explain these data, in this work we have suggested a first approximation model which takes into account the presence of high-density ensembles of grain boundaries in nanocrystalline films and distinguishes the two following basic physical mechanisms of UV-irradiation-induced enhancement of conductivity in the nanocrystalline matter: structural transformations of grain boundaries (which slowly relax) and ionization (which fastly relaxes). A detailed quantitative theoretical analysis and report on a detailed experimental research of these mechanisms responsible for the outstanding ozone sensing properties of InO$_x$ nanocrystalline films under UV light irradiation will be the subject of further investigations.

REFERENCES

[1] *Nanostructured Films and Coatings*, NATO Science Ser., ed. by G.-M. Chow , I.A. Ovid'ko and T. Tsakalakos (Kluwer, Dordrecht, 2000).

[2] *Nanotechnology Research Directions*, ed. by. M.C. Roco, R.S. Williams and P. Alivisatos (Kluwer, Dordrecht, 2000).

[3] H. Gleiter // *Acta Mater.* **48** (2000) 1.

[4] E. Gagaoudakis, M. Bender, E. Douloufakis, N. Katsarakis, E. Natsakou, V. Cimalla and G. Kiriakidis // *Sens. and Act. B* **80** (2001) 155.

[5] M. Bender, N. Katsarakis, E. Gagaoudakis, E. Hourdakis, E. Douloufakis, V. Cimalla and G. Kiriakidis // *J.Appl.Phys.* **90** (2001) 5382.

[6] G. Kiriakidis, M. Bender, N. Katsarakis, E. Gagaoudakis, E. Hourdakis, E. Douloufakis and V. Cimalla // *phys.stat.sol. (a)* **185** (2001) 27.

[7] C. Xirouchaki, K. Moschovis, E. Chatzitheodoridis, G. Kiriakidis and P. Morgen // *Appl.Phys.A* **67** (1998) 295.

[8] C. Xirouchaki, G. Kiriakidis, T.F. Pedersen and H. Fritzsche // *J.Appl.Phys.* **79** (1996) 9349.

[9] H. Fritzsche, B. Pashmakov and B. Clafin // *Solar Energy Mater. Solar Cells* **32** (1994) 383.

[10] D.R. Clarke and G. Thomas // *J.Amer.Ceram.Soc.* **60** (1977) 491.

[11] D.R. Clarke // *Ultramicroscopy* **4** (1979) 33.

[12] W.L. Gong, L.M. Wang, R.C. Ewing and H.S. Xie // *J.Appl.Phys.* **81** (1997) 2570.

[13] M.F. Chisholm and D.A. Smith // *Philos.Mag. A* **59** (1989) 181.

[14] D.R. Clarke // *J.Amer.Ceram.Soc.* **70** (1987) 15.

[15] P. Keblinski, S.R. Phillpot, D. Wolf and H. Gleiter // *Acta Mater.* **45** (1997) 987.

[16] I.A. Ovid'ko and A.B. Reizis // *J.Phys.D: Appl.Phys.* **32** (1999) 2833.

[17] M.Yu. Gutkin and I.A. Ovid'ko // *Phys.Rev. B* **63** (2001) 064515.

[18] V.S. Vavilov, A.E. Kiv and O.R. Niyazova, *Mechanisms for Formation and Migration of Defects in Semiconductors* (Nauka, Moscow, 1981), in Russian.

[19] A.P. Sutton and R.W. Balluffi, *Interfaces in Crystalline Materials* (Claredon Press, Oxford, 1995).

[20] M.I. Buckett and K.L. Merkle // *Ultramicroscopy* **56** (1994) 71.

[21] H. Hilgenkamp and J. Mannhart // *Appl.Phys.Lett.* **73** (1998) 265.

[22] A. Schmehl, B. Goetz, R.R. Schulz, C.W. Schneider, H. Bielefeldt, H. Hilgenkamp and J. Mannhart // *Europhys.Lett.* **47** (1999) 110.

[23] I.A. Ovid'ko // *Mater.Sci.Eng. A* **313** (2001) 207.