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Cost-effective Personal Radiation Dosimetry

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Deep understanding of physical properties of the materials under the influence of radiation exposure is vital for the effective design of dosimeter devices. Detection of radiation is based on the fact that both the electrical and the optical properties of the materials undergo changes upon the exposure to ionizing radiation. It is believed that radiation causes structural defects (called colour centres or oxygen vacancies in oxides) leading to change in their density on the exposure to radiation. The influence of radiation depends on both the dose and the parameters of the films including their thickness: the degradation is more severe for the higher dose and the thinner films.

Thin film technology is considered as cost-effective alternative for a broad range of sensors. However, it is especially attractive for metal oxide films with melting point below 2000 °C, as a wide range of films with mixed composition can be produced. This paper reports on gamma radiation sensing properties of thermally evaporated NbO_2 thin films. These films were deposited at different deposition rate and pressure. It was experimentally confirmed that the manufacturing parameters of the films affected their gamma radiation sensitivity.

Keywords: gamma radiation, thin film, NbO_2, real-time dose monitoring, electrical and optical properties.

INTRODUCTION

Nowadays, more than 20 years later after the Chernobyl tragedy, the true picture of the radiation pollution and its consequences is still not fully known [1]. More than 40 different radionuclides escaped from the stricken reactor, notably in the first 10 days following the accident. The most significant are iodine (I-131), caesium (Cs-137) and strontium (particularly Sr-90). At the time of the accident, there were no dosimetry devices available for civilian use. Inhabitants had to completely rely on the government authorities and their recommendations (if any). Delayed alert of nuclear emergency and unknown level of received radiation dose even more complicated the considerable health and life losses among the population, much of which could have been prevented.

Radiation processing is an expanding technology with numerous applications in, for example, health care products sterilization, sewage and hospital waste treatment, polymer modification and food processing. The effectiveness of the irradiation process depends on the proper application of dose and its measurement. The required absorbed dose range would depend on both the product and the desired effect. Adequate dosimetry with proper statistical controls and documentation is the key factor of the quality control process, which is necessary to assure the products are properly treated.

Real-time radiation detectors become an essential part of emergency personnel who may have to respond to unknown accidents, incidents or terrorist attacks, which could involve radioactive material. More and more ordinary citizens are interested in personal radiation protection as well. Reasons include lost sources, nuclear industrial accidents, nuclear or radiological terrorism and the possibility of nuclear weapons being used in a war. People want to have the ability to measure it for themselves and they want to be notified when the radiation levels are increased.

To meet this demand, considerable research into new sensors is underway, including efforts to enhance the sensor performance through both the material properties and manufacturing technologies. The recent availability of various metal oxide materials in high-surface-area nanopowder form, as well as implementation of newly developed nanofabrication techniques, offer tremendous opportunities for various sensors manufacturers. New preparation technologies and optimized deposition process are essential to achieve better control of the materials characteristics and consequently to improve the radiation sensor performance.

Accordingly, deep understanding of physical properties of the materials under the influence of radiation is vital for the effective design of devices for radiation-sensing applications [1]. Mixing oxides in various proportions was found to control the radiation sensing properties of the semiconductor films in terms of their sensitivity to γ-radiation exposure and working dose region [2].

EXPERIMENTAL PROCEDURE

There are a wide variety of techniques for deposition of thin films. The examples are thermal evaporation (also known as vacuum vapour deposition), electron-beam evaporation, magnetron sputtering, chemical vapour deposition (CVD) and molecular beam epitaxy (MBE) [3 – 6]. Vacuum evaporation is a method used to deposit many types of materials in a highly evacuated chamber. It consists of vaporizing a solid material by heating it to sufficiently high temperatures and re-condensing it onto a cooler substrate to form a thin film. A large current is passing through a filament container (usually in the shape of a basket, boat or crucible) with finite electrical resistance, thus heating the material. The evaporation temperature and its inertness to alloying/chemical reaction with the evaporant dictate the choice of this filament

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material. Once the material is evaporated, its vapour undergoes collisions with the surrounding gas molecules inside the evaporation chamber. As a result, a fraction is scattered within a given distance during their transfer through the ambient gas. The mean free path for air at 298 K is approximately 45 cm and 4500 cm at pressures of 10^{-4} torr and 10^{-6} torr respectively. Therefore, pressures lower than 10^{-5} torr are necessary to ensure a straight-line path for most of the evaporated species and for substrate-to-source distance of approximately 10 cm to 50 cm in a vacuum chamber. The substrates with appropriate masks are placed above and at some distance from the material being evaporated. When the process is completed, the vacuum is released and the masks are removed from the substrates. This process leaves a thin, uniform film of the deposition material on all parts of the substrates exposed by the open portions of the mask.

The vacuum evaporation technique is most suitable for deposition of the materials that are difficult to evaporate in air. The method is clean and allows a better contact between the layer of deposited material and the surface upon which it has been deposited. In addition, because evaporation beams travel in straight lines, very precise patterns may be produced. In general, thermal vacuum deposition produces films with structural defects, such as grain boundaries or lattice imperfections [6]. The so-called minor defects, which are frequently observed in deposited films include dislocation loops, stacking-fault tetrahedral, and small triangular defects; all of these are generally attributed to vacancy collapse [6]. Controlling the deposition conditions such as pressure, deposition rate, substrate temperature and surface nature can alter the intensity of such defects. The settings for the evaporation procedure vary depending on the type of the material being deposited and desired film properties, such as thickness and conductivity.

An Edwards E306A vacuum thermal coating system was used for thin films deposition in a number of our research experiments. The coating unit is equipped with a 550 watt rotary pump and an E040 diffusion pump capable of achieving a vacuum of $5{\cdot}10^{-7}$ mbar. The coating unit consists of a vacuum chamber containing a four-position turret source capable of holding four boats. A shutter is also incorporated, which shields the substrate from evaporants during the outgassing and baking. This system contains an Edwards FTM5 quartz crystal to monitor the rate of film deposition and to measure the film thickness. The quartz crystal was positioned directly above the evaporation source. The mass deposited on the quartz crystal during the evaporation alters its natural frequency of vibration. This frequency change was recorded on the meter of the film thickness monitor connected to the quartz crystal. Thus the monitor could record both the thickness and the rate of deposition corresponding to a particular frequency shift.

Initially, the evaporation chamber was lined with aluminium foil to avoid contamination of and by the surrounding walls. Clean brass masks with suitable apertures were used to deposit thin film structures in required patterns. Devices with cloverleaf geometry, planar-type and layered structures, as well as diodes were manufactured. The materials to be deposited were loaded into tungsten or molybdenum boat of various shapes and sizes, depending on the materials' properties. Then the materials are heated until the evaporation takes place. The settings for the evaporation procedure vary depending on the type of the material being deposited and desired film properties, such as thickness and conductivity.

Figure 1 shows the basic schematic of the overall vacuum evaporation system used for thin films depositions.

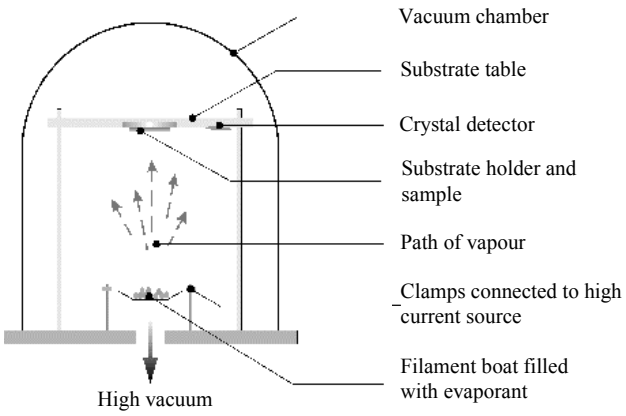

Fig. 1. Vacuum evaporation system

In this work, two types of Niobium oxide (NbO_2) thin films were deposited with the following parameters:

Type 1: NbO_2 powder was baked on a tungsten boat in a vacuum until outgassing was observed to cease, and a stable base chamber pressure of 10^{-6} mbar was achieved. Glass substrates were initially heated to 300 °C for 10 minutes and allowed to cool to 150 °C. The NbO_2 was then heated in the tungsten boat to achieve a deposition rate of 2.5 nm/s at a vapour pressure of $8{\cdot}10^{-6}$ mbar. A film thickness of 98 nm was achieved. Afterwards, the films were annealed in vacuum at 300 °C for two hours. The resultant films exhibited n-type behaviour and had resistance of approximately 4 MΩ.

Type 2: NbO_2 powder was baked on a tungsten boat in a vacuum until outgassing was observed to cease, and a stable base chamber pressure of 10^{-6} mbar was achieved. Glass substrates were held at room temperature. The NbO_2 was heated in the tungsten boat to achieve a deposition rate of 4 nm/s at a vapour pressure of $5{\cdot}10^{-6}$ mbar. A film thickness of 117 nm was achieved. These type 2 films also exhibited n-type behaviour, but the resistance was 400 kΩ – 500 kΩ.

RESULTS AND DISCUSSION

To examine the sensitivity of the oxide films to gamma radiation, they were exposed to a disk-type ^{137}Cs radiation source with an activity of 370 kBq. The radioactive gamma-emitting element was encapsulated into a 2-mm thick high strength epoxy resin to shied any accompanying β-radiation. The source was held at a distance of 10 mm from the surface of the film at an angle of incidence of 0°. The optical properties of NbO_2 thin films were explored using CARY 1E UV-Visible Spectrophotometer.

As one can see from Figures 2 and 3, both types of films showed an increase in the optical density as a result of gamma radiation influence. Moreover, type 2 films were

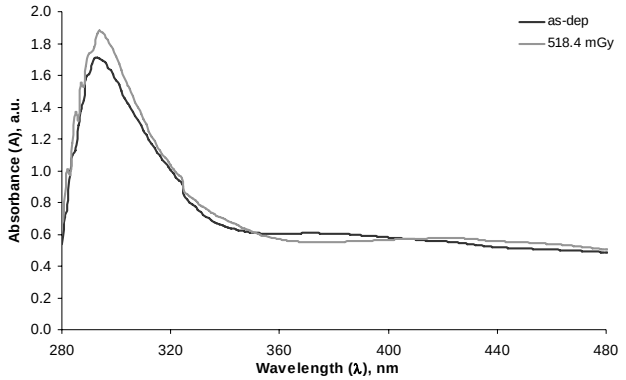

Fig. 2. Change in the optical absorption spectra of NbO_2 (type 1) films under the influence of γ- dose of 518.4 mGy

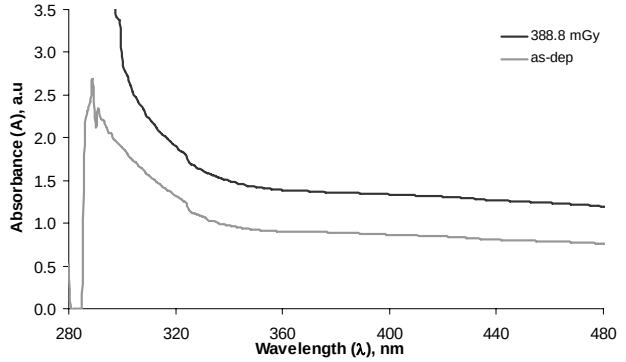

Fig. 3. Change in the optical absorption spectra of NbO_2 (type 2) films under the influence of γ- dose of 388.8 mGy

more sensitive to lower dose of 388.8 mGy, notwithstanding the fact that these films were a bit thicker than counterpart type 1 films. Accordingly, the composition of the film alone also play profound role in their gamma radiation sensing ability. It could be explained by the earlier demonstrated fact that in the composition range from NbO_2 to Nb_2O_5 instable phases $Nb_{12}O_{29}$, $Nb_{22}O_{54}$, $Nb_{25}O_{62}$, and so forth exist [7].

These findings are in line with the results reported earlier for TeO_2 thin films, since the optical properties of thermally deposited TeO_2 thin films having a thickness of 50 nm also showed a high sensitivity to gamma radiation [8, 9]. Typical plots of the absorption spectra for as-deposited and γ-irradiated thin films of TeO_2 are shown in Figure 4. The optical band gap value decreased from 3.75 eV to 3.45 eV with the increase in radiation dose up to 36 Gy. The values of the optical band gap (E_{opt}) for as-deposited and γ-irradiated specimens were estimated using the Mott and Davis' model for the direct allowed transition [10]. The variation in the optical energy gap with irradiation can be explained using the density-of-state model. It is known that E_{opt} decreases with the increase in the degree of disorder of the amorphous phase [11]. At this stage one may expect that a band tail be, probably, created due to irradiation. The decrease in E_{opt} leads to a shift in the band tail ΔE towards the higher energy region and hence the calculated value of ΔE is expected to increase as the radiation dose is increased. Generally, wide band gap compound semiconductors, in particular glassy materials, are of interest for room-temperature ionizing radiation detection. However, pure amorphous materials are preferred over typical glasses. In turn, pure crystalline materials are preferred over the pure amorphous because of their greater number of states and their structural characteristics, such as greater susceptibility to permeation [12].

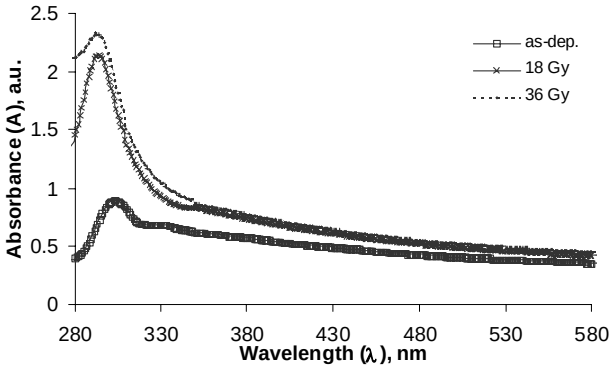

Fig. 4. The absorption spectra for as-deposited and irradiated TeO_2 thin films, © 2003 IEEE [9]

The basic process of nuclear energy loss is the direct transfer of energy to atoms of a solid by elastic collisions between the projectile and the target nuclei. Primary knock-on atoms, set in motion by incident radiation, gain a sufficient amount of energy to subsequently displace other target atoms through secondary- and higher-order collisions [13]. The sequence of energy sharing collisions constitutes a displacement cascade, which could lead to a large variety of structural modifications, i. e. topological or chemical disorder, swelling, polygonization, amorphization [14].

The primary interaction between energetic radiation and semiconductors results in the loss of energy to the electrons, and this energy is ultimately converted to the form of electron-hole pairs. In this process, known as ionization, the valence band electrons in the solid are excited to the conduction band and are highly mobile, if an electric field is applied [15]. The number n of the electron-hole pairs produced is given by E/W, where E is energy absorbed to electronic excitation and W a parameter $2-3$ times the band gap energy [16]. Electron-hole pairs have relatively long lifetimes, unless their concentration is extremely high and Auger recombination dominates. Any atomic process that occurs as a consequence of electronic excitation should utilize the band gap energy possessed by an electron-hole pair, of which the wave functions are delocalized.

The production and subsequent trapping of the holes in oxide films cause serious alterations in the devices performance. Optical absorption analysis has widely proven to be an important and efficient tool in exploring and interpreting the various phenomena of electronic structure and processes in the materials, subjected to radiation [10, 17, 18]. The considerable theoretical investigations on the optical behaviour of thin films deal primarily with optical reflection, transmission, and adsorption properties, and their relation to the optical constants of films [17]. The importance of studying the optical properties of a material is offered by the ability of this technique to provide information regarding the fundamental gap, electronic transition, trapping levels and

localized states. In general, films are amorphous and at most they are polycrystalline in nature.

The change in conductivity caused by the formation of new energy levels under the action of radiation is difficult to estimate, since neither the energy nor the number of new levels is accurately known. The ionizing energy of new levels is high and the low-lying levels may carry out the donor as well as the acceptor impurity effects, owing to this compensating effect. In the initial stage of irradiation, the resistance increases in any material containing donors or acceptors of low ionizing energy. If the irradiation is continued after the compensation of the impurities present in the original crystal, the formation of acceptor levels is permanent. The deep lying energy levels produced by irradiation are very effective recombination centres, which can reduce the carrier lifetimes by several orders of magnitude. These lattice defects generated by radiation damage last at room temperature for several months.

Properties of metal oxides materials are directly or indirectly connected to the presence of defects, oxygen vacancies in particular [19, 20]. These defects determine the optical, electronic and transport properties of the material and usually dominate the chemistry of its surface. Oxygen vacancies are naturally present in every oxide in the form of Shottky or Frenkel defects, and their concentration can be increased or reduced in several ways [20]. This holds not only for bulk properties, but also for the surface of oxides, where several kinds of point defects exist and exhibit a rich and complex chemistry. Depending on the material electronic structure, the nature of oxygen vacancies changes dramatically. Examples include non-metal vacancy at metal/non-metal site, neutral vacancies, positively/negatively charged non-metal vacancies, free positive holes, etc [21].

Oxygen vacancies are known as colour centres, or F centres (from *Farbe*, the German word for colour). It is believed that ionizing radiation causes structural defects, leading to a change in their density upon exposure to γ-rays [22]. Colour centres in oxide thin films, such as WO_3 and MoO_3, have been observed by irradiation with UV light from a high-pressure lamp in the fundamental absorption region at a wavelength of 330 nm [23]. The formation of colour centres has been associated with an increase in electrical conductivity, in which free electrons are produced as a result of band-to-band transitions and trapping of these electrons in oxygen ion vacancies. It was found that there are more than one type of defects responsible for the formation of colour centres in MoO_3 thin films [23].

Alternatively, both sputtered SiO_2 thin films and fused SiO_2 are identical in producing colour centres, especially when they are bombarded by neutrons or X-rays [24]. Miyakawa et al [25] studied the effects of high-energy ions on the $12CaO{\cdot}7Al_2O_3$ films. Reportedly, the conductivity of the films was enhanced and the films become coloured by irradiating with ultraviolet light due to the formation of F^+-like centres. The electrons forming the F^+-like centres are photo released from the encaged H^- ions, which are presumably derived from the pre-existing OH^- groups. The induced electron concentration was proportional to the calculated displacements per atom, which suggests that nuclear collision effects of the implanted ions played a dominant role in forming the electron and H^- ion in the films [25].

The influence of gamma radiation on In_2O_3/SiO films resulted in significant changes in the microstructure of these films. Some kind of agglomerations with variable sizes in the range $0.5\ \mu m - 3\ \mu m$ occurred [26]. After a dose of 8160 μGy, evidence of partial crystallization was observed with the use of X-ray diffraction. Most of the radiation-induced defects are due to oxygen vacancies that to a certain extent cause degradation in the stoichiometry of the layers.

Crystal structure and optical properties of TeO_2 were the subjects of numerous theoretical and experimental studies [27,28]. Tellurium dioxide belongs to the category of compounds in which all the atoms are the so-called *p*-elements, having non-bonding valence electron pairs. TeO_2 and almost all the Te^{IV} containing compounds (including the glasses), exhibit remarkable properties related to macroscopic polarization and polarisability (dielectric, piezoelectric, optic, electro-acoustic), which are of great interest for the fundamental science and technology. The origin of such properties, particularly for TeO_2-based materials is related to the peculiarities of the electron distribution inside the coordination polyhedra. According to Raman spectrum studies, TeO_2 thin films experienced structural alterations after their exposure to radiation, indicating further transformation to γ-TeO_2 modification [26].

It is generally accepted that two distinct processes are responsible for the formation of colour centres, following bombardment with ionizing radiation. The primary mechanism is in charge for defect formation, while the secondary one gives rise to the stabilization of the centres [29]. The model for colour centre kinetics assumes that the level of the radiation damage should be dose rate dependent, because of the damage recovery [30]. As colour centres are created under irradiation, they also annihilate even under room temperature. During irradiation, both annihilation and creation coexist. The colour centre density will reach equilibrium at a level, depending on the applied dose rate. The creation and annihilation constants can be determined by using experimental data obtained under one particular dose rate, and can then be used to predict the behaviour of the same sample under different dose rates [30].

Detection of radiation was based on the fact that electrical, optical and structural properties of the materials undergo changes under the influence of gamma radiation. The influence of radiation depends on both the dose and the parameters of the films including their thickness: the degradation is more severe for the higher dose and the thinner films. Values of radiation damage in the samples were estimated from changes in their current-voltage characteristics and the optical absorption spectra, which were recorded after each exposure procedure.

CONCLUSIONS

NbO_2 and TeO_2 thermally evaporated thin films were explored as candidates for cost-effective personal radiation sensors. The properties of these films were highly affected by the influence of radiation. The degree of changes caused in their optical properties was correlated with the level of gamma dose and also depend on the materials

properties and parameters of the films. Thus, the sensitivity range of the metal oxides thin film sensors can be tailored for a particular application.

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