NANOPOROUS ALUMINUM OXIDE AS A THERMOLUMINESCENT SENSOR FOR IONIZATION RADIATION.

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Abstract. In this work we investigated the thermoluminescence proprieties of nanoporous aluminum oxide strips produced by anodic oxidation of aluminum in several solvents in order to obtain a suitable dosemeter for radiation dose measurements. The photoluminescence and infrared characterization were performed at room temperature using a Jobin Yvon Ramannot model U-1000 spectrometer using either a 150 W Xe Lamp or a argon laser as a excitation source. The dosimetric proprieties of the nanoporous aluminum oxide strips were studied in order to determine their usefulness as thermoluminescent dosemeters. The samples were tested in X radiation beams and evaluated in relation to their main dosimetric characteristics, as TL glow curves, calibration curves and energy dependence. The TL readouts were performed with a 2800M Victoreen reader under a linear heating rate of 8°C/s up to 320°C and all samples were annealed for 1h at 400°C before each irradiation. The results showed a linear TL response with the dose in the range from 100mGy to 1100mGy.

1. Introduction

Nanotechnology research, to a great extent is based on fabricating functional nanoscale structures and devices in a well-controlled way, which represents one of the most difficult challenges facing today’s researchers and engineers. The means to organize nanoelements into device structures in order to realize their desired functionalities, using inexpensive fabrication techniques, is essential from a technological point of view. Due to the small dimensions of these nanoelements, a bottom-up self-assembly process often provides a viable approach to overcome such technological challenges [1,2]. One of the important aspects of self-assembly lies in its capability of forming a large area of uniform structures through inexpensive chemical or biological processes. A major concern of using self-assembly processes to fabricate nanoscale devices for electronic or optoelectronic applications is their compatibility with high-vacuum and high temperature technologies. Most electronic and optoelectronic devices are based on high-quality semiconductors, and their production involves complicated micro or nanofabrication processes. It will be highly beneficial if the self-assembly nanofabrication techniques can be combined with traditional silicon microfabrication technologies in the pursuit of next-generation high-performance nanoscale devices.

Aluminum anodization [3] is one of the most controllable self-assembly processes, and nanoporous anodic aluminum oxide has been employed to synthesize a variety of nanoparticles and nanowires through a template-mediated approach [4]. The electrochemical self-assembly consist of basically three steps: (a) electro-polishing an aluminum foil in a suitable electrolyte to clean and prepare the surface, (b) anodizing the electropolished foil in a desired solvent with a dc current to form a porous alumina film on the surface, and finally (c) electrodepositing or chemically synthesizing the material of interest within the pores. Recently, aluminum anodization has been combined with traditional silicon processing to fabricate uniform anodic aluminum oxide thin films directly onto a silicon substrate [5], and it was also used to produce planarized microelectronic components from aluminum and anodic alumina layers on large scale of integration and hybrid circuits such as interconnections, inductors, capacitors and others [6-9].

On the other hand another interesting problem to be solved is the manufacturing of reliable dosemeter to be used in the radiation ionization field. The increase use of ionization radiation in the diagnosis and therapy of some diseases, as well as the modern radiation diagnosis and radiotherapy equipment available make necessary the use of a highly reliable dosimeter which is able to measure more and
more low energy radiation. One of the former materials studied for possible use as a dosimeter is aluminum oxide (Al$_2$O$_3$). However, the study of this material was forgotten for a long time, because of its low sensibility compared with that of TLD-100.

Recently the interest on this materials increase due to the development of anion defective Al$_2$O$_3$:C single crystals, which prove to be more sensitive than TLD-100, however, the well established crystal growth technique require a sophisticated laboratory infrastructure at high temperature, using a highly reducing atmospheres, some time not available in common laboratory. In this paper, we will present the development of a straightforward route to prepare a highly sensitive thermoluminescent carbon doped nonporous aluminum oxide at low temperature using the anodization process in diverse solvents and discuss the photoluminescent and thermoluminescent results as a function of the synthesis medium.

2. Experimental Procedure

The anodizing aluminum oxide (AAO) template was generated with high purity aluminum foil (99.99%) in acid solution using a two step process [10]; the process was carried out either at a constant voltage of 40 V in 0.3 M organic acid solution at 10 °C or at 18 V for 0.5 M of inorganic acid. After the first anodization, the oxide film was removed and the newly patterned aluminum substrate was anodized again. The time was determined by the required thickness of the AAO film, finally the AAO doped films were thoroughly washed with deionized water and put into a furnace for annealing treatment. The photoluminescence and infrared characterization were performed at room temperature using a Jobin Yvon Ramanor model U-1000 spectrometer using either a 150 W Xe Lamp or a argon laser as a excitation source. The emission light was detected by a water cooled photomultiplier RCA C31034-02 and processed by the Jobin Yvon spectralink data acquisition system, and a FTIR Bruker IF 66 spectrophotometer respectively. A Siemens D-5000 X ray diffractometer with a Cu target was used to obtain the X-ray diffraction patterns of the samples.

To study the dosimetric proprieties of the nanoporous aluminium oxide samples, they were irradiated in presence of the TLD-100 dosemeters with a X-ray beam from 8 to 18 keV, in a range from 100 mGy to 500mGy. Prior to each irradiation the samples were thermally treated at 673K (400°C) for 60 minutes, in order to erase any remaining information. The readings of thermoluminescence were carried out in a Victoreen 2800M equipment with a heating form room temperature to 433K (160°C) in 10 sec and than a linear heating rate of 8K s$^{-1}$ up to 593K (320°C) in 20s was applied. For TLD-100, the readings of thermoluminescence were carried out in the same equipment with a heating from room temperature to 433K (160°C) in 10 sec and than the sample was heated to 573K (300°C) in 10s.

3. Results and discussion

The structural characteristics of nanoporous aluminum oxide films synthesized by the anodization process in oxalic acid is illustrated in Figure 1, where X-ray diffraction patterns for the undoped film without annealing treatment are shown. These patterns shows several peaks associated with Al and Al$_2$O$_3$ crystalline phases on top of a broad peak centered at 20 ~ 25 degrees. The broad peak is indicative of a highly disordered and/or amorphous aluminum oxide compound.
The IR spectra of aluminum oxide film prepared in organic acid (full curve) and inorganic acid (broken curve) are compared in Figure 2. Both spectra have absorption bands at about 3400 cm$^{-1}$ and in the region 1250-400 cm$^{-1}$. The former is due to the O--H stretching vibration of the bound water within the film. The latter is due to the intrinsic vibrations of the alumina constituting the bulk of the film the band with a peak at 1246 cm$^{-1}$ observed with the inorganic acid film, is assigned to the vibration arising from sulphate species incorporated into the film during anodization, and the band observed at 1107 and 1032 cm$^{-1}$ in inorganic acid can be assigned to the coupling of the C-C stretching vibration and the O-C=O bending vibration.

The double absorption band with peaks at 1634 and 1485 cm$^{-1}$, observed with the organic acid film and absent for films formed in inorganic acid electrolytes, can be reasonable assign to the antisymmetric O--C--O stretching vibration; and to the coupling band arising from the symmetric O--C--O stretching vibration and the C--C stretching vibration respectively. Accordingly, it seems quite reasonable to assume that the double absorption band is inherent to the films formed in aliphatic carboxylic acid solutions and is due to carboxylate species incorporated into the films during anodization.

Fig. 1. X-ray diffractogram of anodized aluminum oxide synthesized in organic acid 0.3 M.
Fig. 2. Comparison between the IR reflection spectra of the organic acid (solid line) and inorganic acid films (dot line)

The photoluminescence emission spectra for the unirradiated nanoporous aluminum oxide prepared in organic acid are shown in Figure 3. We can see two unexpected broad peaks, one at 429 nm and the other at 491 nm when the sample is excited by UV at 320nm. It is interesting to mention here that these unexpected peaks do not appear in the emission spectra of the sample synthesized in inorganic acid suggesting that probably these peaks are related with the presence of F centers and/or free radicals of carbon related centers, as shown in the infrared spectra.

Fig. 3. Room temperature photoluminescence emission from nanoporous aluminum oxide excited at 320 nm

The glow curves from two carbon doped nanoporous Al2O3:C samples irradiated with X-ray 80 Kv, at room temperature with are shown in Figure 4. One can see that for the untreated sample the glow curves are characterized by two-glow peak, one at 370 K and the other at 490 K. When the sample is annealed at 873 K for 24 h and irradiated with X-ray 30K, Figure 5, one observes that only one peak
remains at 493 K, also we observe that the glow response for the annealed samples is more intense. The reason for the appearance of two glow peaks may be related with free radicals of carbon related centers adsorbed on the nanoporous Al₂O₃ surface, since the samples is synthesized in organic acid, for the sample prepared in inorganic acid the thermoluminescence is too much low and is comparable with the undoped Al₂O₃ single crystal. Now when the sample is annealed, probably the organic radicals is decomposed and the two valent ions of carbon impurity are supposed to replace three valent cation of Al in the oxide lattice which leads to the formation of hole trapping centers, for that reason we may assign the first glow peak for the untreated sample to the organic free radical, which disappear with the heating treatment.

(a) Untreated sample                                               b) Sample annealed at 873 K for 24 h

Fig.4- The glow curves from two carbon doped nanoporous Al₂O₃:C samples irradiated with X-ray 90 Kv, at room temperature

The reproducibility of the TL response of carbon doped nanoporous Al₂O₃:C dosimeter was obtained from 10 readings after repeated procedures of standard annealing and irradiation. The standard deviation was 3.4 %

The Figure 5 shows the TL dose response of carbon doped nanoporous Al₂O₃:C irradiated with X ray beam in the range from 100 to 11000mGy. The results show a linear relationship between the TL emission intensity of main peak and the dose, for the investigated dose range. The correlation coefficient (r²) and the equation of the calculated linear function of each interval were calculated and are shown in Table 1.
Fig. 5- The dose response to X-ray radiation for the main glow peak of carbon doped nanoporous Al2O3:C

Table. 1 –Correlation coefficient (r²) and slope (b) for linear regression for each energy used

<table>
<thead>
<tr>
<th>KVP</th>
<th>r²</th>
<th>Equation</th>
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<tr>
<td>30</td>
<td>0.996</td>
<td>Y(a.u.)= 0.67.X(mGy) +2.5</td>
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<tr>
<td>50</td>
<td>0.9943</td>
<td>Y(a.u)=0.5206.X(mGy)+0.58</td>
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<tr>
<td>60</td>
<td>0.9998</td>
<td>Y(a.u)= 0.5108.X(mGy)+41.47</td>
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<tr>
<td>80</td>
<td>0.9965</td>
<td>Y(a.u)=0.8069.X+102.6</td>
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5. Conclusion.
The straightforward methods to produce carbon doped nanoporous aluminum oxide strips and their linear dose response indicate that this material presents a high potential to be used for radiation dosimetry.

6. Acknowledgements
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7. References