

Relaxation of Photoconductivity and Persistent Photoconductivity in TiO₂ nanotubes

Mihail ENACHI, Tudor BRANISTE, Eugeniu BORODIN and Vitalie POSTOLACHE

National Center of Material Study and Testing, Technical University of Moldova, Stefan cel Mare av. 168, Chisinau MD-2004, Republic of Moldova, e-mail: enachim2002@yahoo.com

Abstract — Relaxation of photoconductivity is investigated in titania nanotubes produced by electrochemical treatment of Ti foils in organic electrolytes with subsequent thermal treatment at 400 °C in air. The photoconductivity was excited both in air and in vacuum with the radiation from a xenon lamp passed through different filters to vary the excitation intensity and wavelength. It was found that the photoconductivity relaxation process consists of two components, i. e. a fast component a slow one. These two components behave differently in air and in the vacuum. The fast component is even faster under vacuum, while the slow component in vacuum is much slower, therefore leading to persistent photoconductivity. The possibility of removing the persistent photoconductivity state by exposure to air is investigated.

Index Terms — Titania nanotubes, relaxation of photoconductivity, persistent photoconductivity.

I. INTRODUCTION

Titanium dioxide is a thermally and chemically stable, nontoxic advanced compound with various applications as sensor [1,2] or luminescent material [3], or in photochemical [4,5] and photovoltaic devices [6,7]. All these applications are impacted by electrical and photoelectrical properties of the material, particularly by the mechanisms of photoconductivity relaxation and persistent photoconductivity.

It is known that in nanostructured oxide materials such as ZnO [8,9] and TiO₂ [10,11], these properties are strongly influenced by the band-gap electronic states arising from oxygen vacancies, and surface states due to adsorbed oxygen. In TiO₂ nanotubes such states may also be located at their huge surface and may determine, in part, electron transport in the material.

Oxygen vacancies, which are intrinsic for any oxide material, are the result of an equilibrium formatted between neutral oxygen molecules in the gas phase and oxygen anions in the lattice [11]. A large number of surface states have been found in nanostructured TiO₂ [12]. These states can create surface bands and significantly alter the surface band-gap properties with respect to those of the bulk material. A number of bulk and surface states are possible within the band gap for titanium dioxide. There exist 0.75 and 1.18 eV states (electron trapped at a single-charged and double-charged oxygen vacancy, respectively) [13]. It was previously observed that all surface defects in nanostructured anatase TiO₂ are affected by oxygen adsorption in oxygen containing ambient [10].

In this paper we investigate the relaxation of photoconductivity in TiO₂ nanotubes excited with radiation of various intensity and wavelengths from a Xe lamp.

II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

Titania nanotubes have been produced by electrochemical treatment of Ti foils in organic electrolytes. The samples were subjected to thermal treatment in air at 400 °C. Ohmic contacts were formed by deposition of an InGa alloy. The radiation of a xenon lamp with spectrum shown in Fig. 1 was used for photoconductivity excitation.

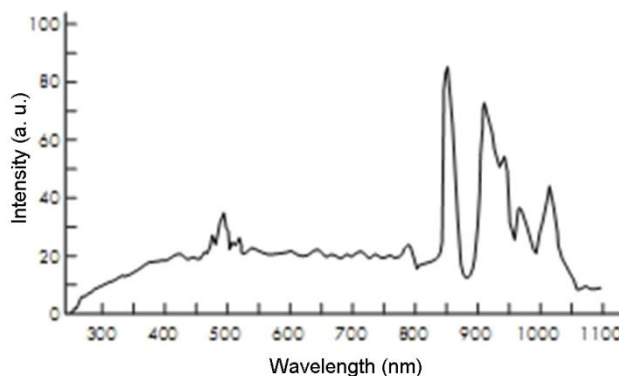


Fig. 1. Spectrum of a xenon lamp used for excitation.

The radiation from the lamp has been passed through neutral filters with spectral characteristic shown in Fig. 2 in order to vary the intensity of excitation.

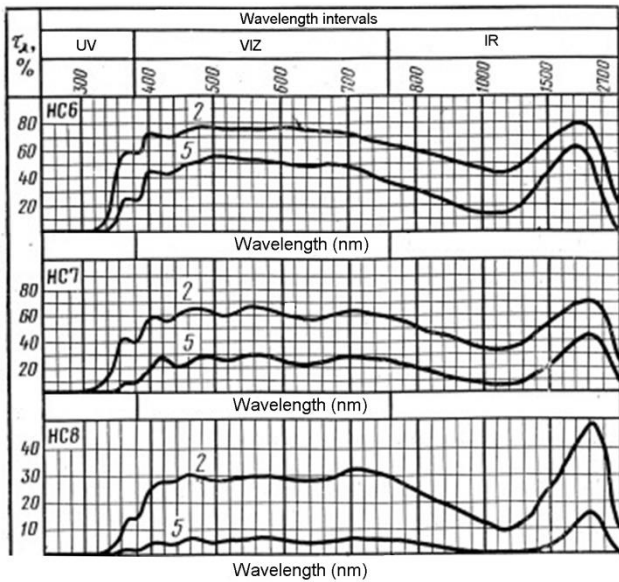


Fig. 2. Spectral characteristics of neutral filters used for decreasing the intensity of the excitation.

Filters with spectral characteristics illustrated in Fig. 3 were employed to select excitation wavelength from the UV or visible range, while filters with spectral characteristics shown in Fig. 4 were used to select radiation with wavelength from the IR diapason.

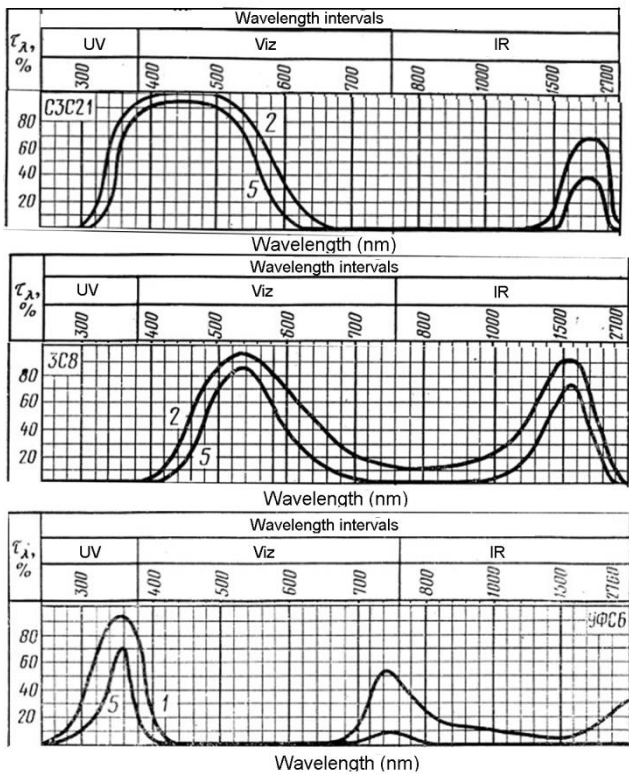


Fig. 3. Spectral characteristics of filters employed to select excitation wavelength from the UV or visible range from a xenon lamp.

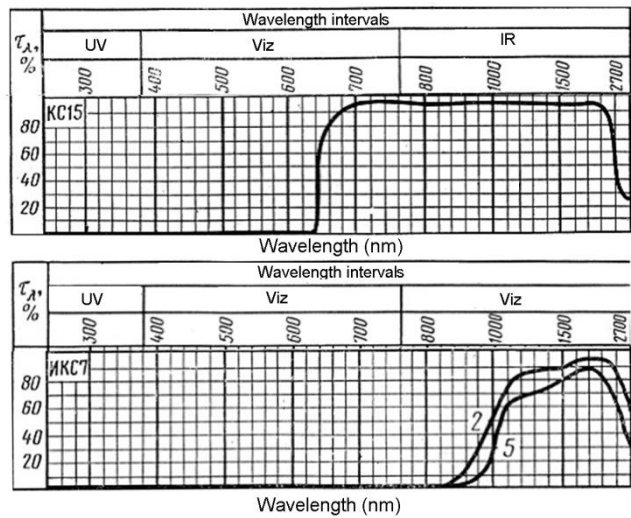


Fig. 4. Spectral characteristics of filters used to select radiation with wavelength from the IR diapason.

III. RESULTS AND DISCUSSIONS

Figure 5 demonstrates linear current-voltage characteristics both in darkness and under illumination, which is a confirmation that the deposited contacts are ohmic.

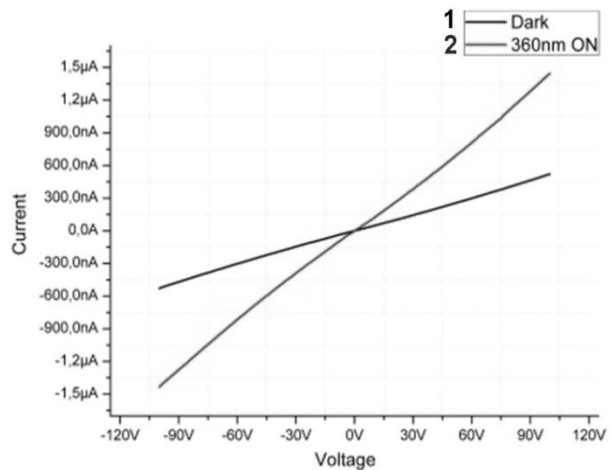


Fig. 5. Current-voltage characteristics of TiO₂ nanotubes at 300 K.

The built-up and the decay of photoconductivity of TiO₂ nanotubes measured in air under the excitation with integral radiation from a xenon lamp are shown in Fig. 6. One can realize from this figure that the photoconductivity decay consists of two components, i. e. a fast component and a slow one. The fast component is within a minute, while the fast one lasts for many ours. A second cycle of excitation with the same radiation in a moment of time before the total relaxation of the photoconductivity leads to a similar effect, but the reached value of the photocurrent is higher as compared to that from the first excitation cycle.

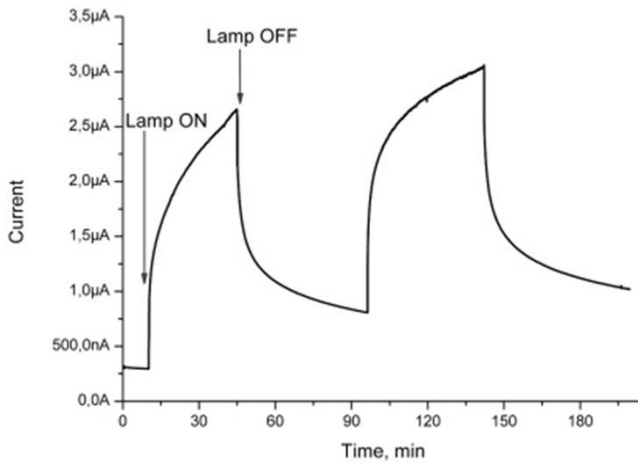


Fig. 6. Built-up and relaxation of photoconductivity in TiO₂ nanotubes and excitation in air by the integral radiation from a xenon lamp.

The evacuation of air results in a considerable increase of the dark current that means that the resistivity of the sample decreased. This effect is most probably related to the desorption of the oxygen from the surface of titania nanotubes. This behavior is typical for oxide semiconductors in air. The relaxation of photoconductivity in vacuum is also different from that in air (Fig. 7). The fast component of relaxation in the vacuum is even faster, it being in the limit of seconds, while the slow component is much slower as compared to the relaxation in air, it leading to persistent photoconductivity.

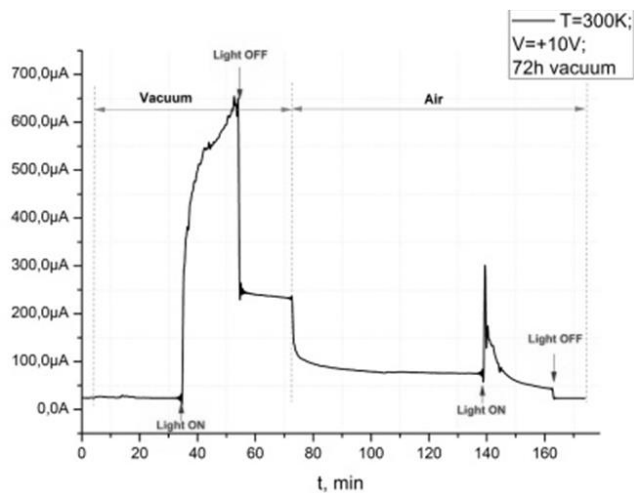


Fig. 7. Built-up and relaxation of photoconductivity in TiO₂ nanotubes and excitation in vacuum by the integral radiation from a xenon lamp followed by the introduction of air and a second excitation with the radiation from the xenon lamp.

As expected, the introduction of the air leads to the decrease of the current due to the increase of resistivity. However, the persistent photoconductivity state of the sample seems to be preserved. This is indicated by the value of dark current several orders of magnitude higher than the initial dark current in Fig. 6, as well as by absolutely different behavior under the photoexcitation.

Instead of a usual photocurrent built-up and relaxation observed in Fig. 6, there is a current spike followed by a gradual decrease of the current under the excitation from the xenon lamp. As a result of this excitation, the sample is transferred into a new state with the dark resistivity nearly equal to that of the initial dark conductivity in vacuum. As shown in Fig. 8, the slow component of photoconductivity relaxation in air is absent in this state, while the behavior in vacuum is similar to the previous one. The photoexcitation in vacuum leads again to a persistent photoconductivity state, while the introduction of air and the photoexcitation leads to the repetition of the cycle (see Fig. 8).

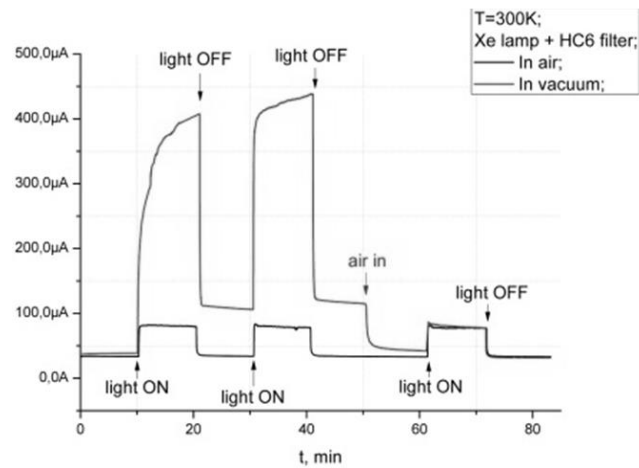


Fig. 8. Built-up and relaxation of photoconductivity in TiO₂ nanotubes under a repeated excitation in air and in the vacuum with the radiation from a xenon lamp passed through a HC6 optical filter.

The investigation of photoconductivity of titania nanotubes under excitation with radiation from the xenon lamp passed through different filter (Fig. 9) suggests that the photoconductivity is mainly extrinsic, since it is strongly excited by the IR light produced by radiation passed through the KC15 and ИКС7 filters, while it is hardly excited by the intrinsic UV light produced by radiation passed through the УФС6 filter.

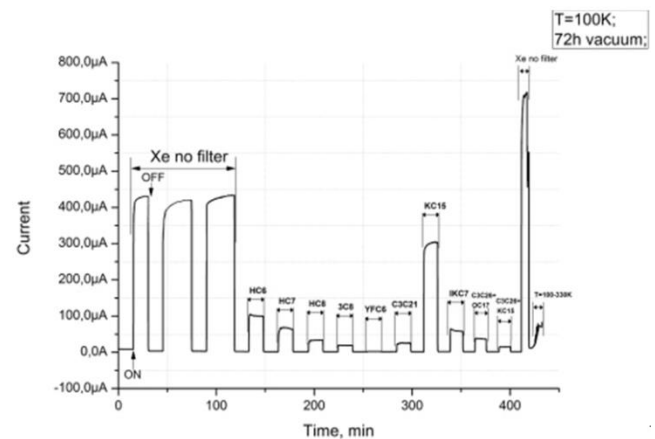


Fig. 9. Photoconductivity of titania nanotubes under excitation with radiation from the xenon lamp passed through different filters.

IV. CONCLUSIONS

The results of this study demonstrate a different photoconductivity relaxation in air and vacuum for titania nanotubes produced by electrochemical treatment of Ti foils in organic electrolytes with a subsequent thermal treatment at 400 °C in air. The resistivity of samples decreases by several order of magnitude in vacuum as compared to air which is most probably due to the desorption of oxygen from the surface of nanotubes in the vacuum. The photoconductivity relaxation process consists of two components, i. e. a fast component and a slow one, both in vacuum and air environment. However, these two components behave differently in air and in the vacuum. The fast component is even faster in the vacuum, while the slow component in vacuum is much slower, therefore leading to persistent photoconductivity. There are several conductivity and photoconductivity states induced by the air or irradiation in TiO₂ nanotubes. The evacuation of air results in a low resistivity state, while irradiation with visible or near IR light in vacuum induces a persistent photoconductivity state. The exposure to air of this persistent photoconductivity state leads to a new higher resistivity persistent photoconductivity state, which is transformed into another state by irradiation. The last state is different from any of previous ones. This cycle of states can be repeated by evacuation, air exposure and irradiation. The presence of several conductivity states at room temperature in titania nanotubes opens new prospects for the development of switches based on this material. Additional investigations are needed to identify the mechanism of these transformations, since the processes are rather complex due to the fact that oxygen molecules can be adsorbed and desorbed from the surface of titania nanotubes as various species such as negative O₂⁻ ions, O₂²⁻, or O⁻ species.

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