BAND GAP PERSISTENT PHOTOCONDUCTIVITY IN SNO_2 NANOSCRYSTALLINE FILMS: NATURE OF LOCAL STATES, SIMULATION AND COMPARISON WITH EXPERIMENT

Ph.D. V. Brinzari[1], D.Sc. G. Korotcenkov[1], Ph.D. I. Damaskin[2]

[1]Moldova State University, [2]Institute of Applied Physics Moldavian Academy of Sciences
Republic of Moldova, Chisinau
vrinzari@mail.ru

A numerical model of PPC by photon energy excitation below fundamental band gap for nanoscale SnO_2 at room temperature is proposed. PPC considers the concept of surface local states caused by oxygen vacancies and near-surface barrier induced by ionosorbed oxygen. The factors explaining some behaviour details and the discrepancy between the model and the experiment are analyzed.

Keywords: nanoscale SnO_2, persistent photoconductivity, oxygen chemisorption, modeling of photoresponse.

Tin dioxide is a well-known conductive metal oxide with a wide band gap (3.6 eV). Like with other metal oxides, the interest in profound research of this material is linked to high expectations in the field of high-temperature micro- and optoelectronics and gas sensor technology. Ultraviolet photosensitivity is promising area of application for semiconductors with wide band gap. However, the effect of so-called persistent photoconductivity (PPC) which is characteristic for most conductive metal oxides (MOX) [1—4] and even non-oxide materials in many cases limits their usage. Despite a rather intensive research of such effect in SnO_2, detailed understanding of processes governing persistent photoconductivity is still missing [5]. The main idea of present report is to develop a quantitative model of band gap PPC at room temperature, which will be consistent with experimental observations of our research and with results of recent careful spectroscopy study of PPC on SnO_2 films in the spectral range of 2.5—3.3 eV [6, 7].

The authors propose a phenomenological model of room temperature (RT) photoconductivity in nanocrystalline SnO_2 under photon excitation below the fundamental adsorption edge based on electronic states located at the bottom part of the band gap. Nature of these states is related to the surface oxygen vacancies and Sn-derived electronic states. These quasi-continuous electronic states are mainly positioned at the bottom part of the band gap. The synchrotron light photoemission (PE) spectra within band gap binding energies (BE) measured for our films deposited by spray pyrolysis method have proven this characteristic feature. Appropriate distribution of these states was considered in the model.

The important part of the PPC mechanism is the separation of excited electrons and holes by surface potential barrier at the grain boundaries. These potential barriers are caused by the presence of ionosorbed oxygen. Unlike the PPC with excitation energy above the band gap, the hole states are immobile in this considered case. More precisely, these barriers and their magnitudes determine the extra large decay times at room temperature. Numerical simulation of the photoconductivity response and decay on the basis of balance rate equation for excited electrons and immobile holes was done. The strict analysis revealed that response time is determined by the photoionization cross section of these states and intensity of illumination. Stationary photoresponse is saturated due to the limited number of these states. Intergrain potential barrier that originated due to the ionosorbed oxygen is the main factor limiting the reverse annihilation process and determining the photoconductivity decay time. Stretched exponential behavior of the photoconductivity decay was interpreted in terms of structural and electronic film disordering that results in asymmetric probability distribution of the intergrain barrier heights and corresponding distribution of time constants. The dispersion of grain sizes and oxygen inhomogeneous incorporation into the film volume (related with a prehistory of sample preparation) cause these effects.

In the framework of this research, the following findings and conclusions can be formulated:

— it was confirmed by PE spectroscopy that band gap electronic states are due to the defect chemistry of the surface and is related to the presence of surface O-vacancies and Sn-derived electronic states from the dangling bonds;

— mechanism of RT band gap PPC of nanogranular SnO_2 is governed by these electronic states and "frozen" ionosorbed oxygen that forms the intergrain potential barriers;

— magnitude and transient behavior for the photoresponse was simulated and these characteristics are in rather good agreement with experimental observations ;

— detail study of photodecay dependence allows to calculate through the inverse Laplace transform the distribution of intergrain potential barrier heights;

— it was found that the asymmetric distribution of intergrain potential barrier heights is determined by the inhomogeneity of film structure and can be used as a method for film's characterization.

The report presents the obtained experimental photoemission and photoconductivity characteristics for aforementioned spectral region of nanoscaled SnO_2 and results of their simulation.

We believe that this approach is valid not only for tin dioxide, but also for a wide range of conductive metal oxides.

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В. И. Брынзарь, Г. С. Коротченков, И. А. Дамаскин

Долговременная внутризонная фотопроводимость наноразмерных пленок SnO_2: природа локальных состояний, моделирование, сравнение с экспериментом

Предложена численная модель долговременной внутризонной фотопроводимости (ДВФП) для наноразмерного SnO_2 при комнатной температуре. Модель рассматривает возбуждение фотонами с энергией меньше фундаментального края поглощения. Типичное время ответа и затухания ДВФП находится в интервале 10^4—10^6 с. В рамках модели поверхностных электронных состояний, обусловленных вакансиями кислорода и приповерхностного барьера, связанного с хемосорбированным кислородом, удается количественно описать величину фотоответа и соответствующее время переходных процессов при оптическом возбуждении указанного рода. Проанализированы факторы, объясняющие некоторые детали поведения и расхождения модели с экспериментом. Так называемое растянутое экспоненциальное поведение затухания фотоответа отражает разупорядоченность наноструктуры и может быть использовано при определении дисперсии высоты потенциальных барьеров между нанокристаллитами в пленке.

Ключевые слова: наноразмерный SnO_2, долговременная фотопроводимость, хемосорбция кислорода, моделирование фотоответа.