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Application of optical and luminescent techniques to the characterization of oxide thin films

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Abstract

The interaction between light and electrons in oxide compounds forms the basis for many interesting and practical effects, which are related to microstructure, energy band, traps, carrier transport and others. Thin films of oxides like WO_3, Ga_2O_3, Y_2O_3 and $SrTiO_3$ were investigated using various improved optical and luminescent techniques. The home-made systems for optical and luminescent measurements were described in detail. The facilities of photo-Hall and photoconductivity transients have been proven to be powerful tools in the studies, which allow us to perform photoinduced process and relaxation measurements over a wide time range from 10^{-8} to 10^{4} s. Furthermore, we extended the measurement capabilities of the commercial luminoscope by using an interferometer system with optical fiber and illuminance meter instead of an optical microscope. The cathodoluminescent measurements can be performed at a relative high pressure (20–60 mTorr) compared to ultra-high-vacuum condition of most commercial products. Luminescent characterization was employed as a probe to study doping ions, oxygen vacancies, trap and/or exciton levels in oxide thin films. Our results suggest that various traps and/or excitons in thin films of WO_3, Ga_2O_3 and $SrTiO_3$ involve in the process of photoconductivity relaxation and emission.

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Keywords: Characterization; Photoconductivity; Luminescence; Oxide thin films; Trap

1. Introduction

Numerous materials have been prepared in the form of thin films because of their potential technical value and scientific curiosity in their properties [1]. Thus, determining the details of the properties in thin films is not only fundamental to the understanding these materials, but also tailoring the properties to suit applications in microelectronic and optoelectronic devices. Optical and luminescent methods are well established as nondestructive and flexible techniques to characterize different types of oxide-based thin films. A thorough study of the observed effects provides an opportunity to evaluate the different energy bands, trap levels, carrier transport, doping ions and others in oxide thin films.

Photoconductivity is one of basic phenomena related to the interaction between light and electrons in those compounds. The measurement of only photoconductivity in most of previous reports is not sufficient to understand the carrier transport mechanism because conductivity is a product of the mobility and carrier density. Furthermore, the relaxation behaviors of the photoconductivity are very useful to realize the transport mechanisms and test new materials [2–4]. Relaxation time can be ranged from nanoseconds to several days. In this work, the home-made systems of pulsed and steady-state photoconductivity along with photo-Hall measurement were used to determine the properties of photoconductivity and relaxation over a wide time region. In addition, cathodoluminescent (CL) measurements were commonly performed in apparatus with ultra-high-vacuum (UHV) chamber designed originally for other measurements such as scanning electron microscope (SEM). Here we will describe an inexpensive system for the CL measurement performing at a relative high pressure.

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2. Experimental details

2.1. Optical measurements

Fig. 1 shows a home-made setup used for both steady-state photoconductivity and photo-Hall effect measurements. The samples with a Hall-effect pattern were mounted in a cryostat between the poles of an electromagnet at field strength of 0.6 T. Both dark and light measurements were made. The light source was a metal-halide arc lamp (Welch-Allyn). A quartz optical fiber conveyed the radiation from the lamp to the sample in an evacuated chamber. Precision in the highly resistive samples was usually limited by the shot noise. This system was also used to measure slow relaxation behaviors of photoconductivity.

The third harmonic of an Nd:YAG laser ($\lambda = 355$ nm) was used as an excitation source in the measurements of fast photoconductivity transients. The pulse repetition frequency was 5 Hz with a pulse width of 6 ns. The intensity of the laser pulse was 1.15 mJ cm^{-2}. The photoelectric signal across a 50 Ω resistor was recorded by an oscilloscope (Textronix TDS-320), which was triggered by a silicon photodiode. Software was written to enable the oscilloscope to collect averaged data automatically at several scales for both intensity and time.

2.2. Luminescence measurements

A mercury arc lamp along with a monochromator was used as the excitation source for the photoluminescent (PL) measurement. For the CL measurement, a home-made system was performed as shown in Fig. 2. We extended the measurement capabilities of a commercial CL luminoscope (Relion Industries ELM-2B) by using UV/visible interferometer system with optical fiber and illuminance meter instead of an optical microscope. Flexible fiber optic spectroscopy is a low-cost and high-performance system and lets one bring the instrument to the sample flexibly. The CL spectra were measured using an Ocean Optics S2000 CCD spectrometer with a 400 μm diameter single-strand UV/VIS optical fiber. Spectral resolution of the spectrometer was 1.5 nm. The beam

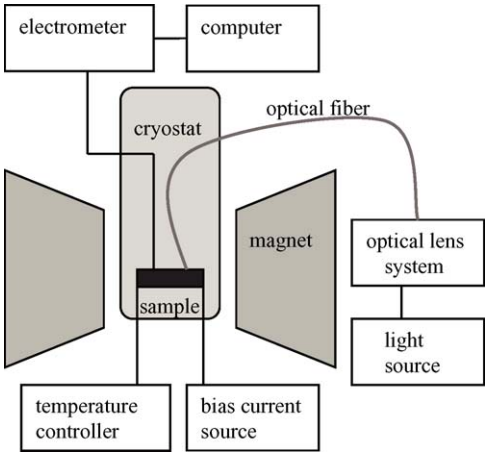

Fig. 1. Measurement set-up for the study of steady-state photoconductivity and photo-Hall effect.

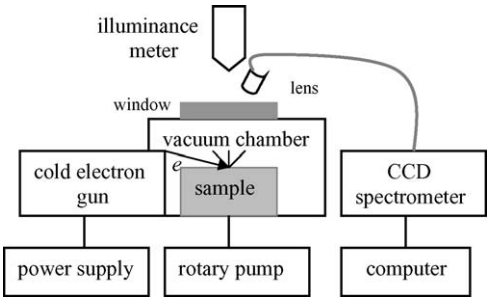

Fig. 2. Schematic diagram of apparatus for the CL measurement.

voltage of a cold cathode electron gun ranged from 4 to 10 kV with a beam current of 0.5 mA in a vacuum chamber to about 20–60 mTorr. Due to the beam scattering in the chamber, the effective current density on the sample was measured to be 62 μA/cm^2 under the typical condition. An illuminance meter (Minolta T-1M) was used to measure the luminance of the films. Loading several samples on the sample holder, which was controlled by a x–y positioner, facilitated measuring the emission of the samples in sequence under the same conditions. A metal mask with a hole was placed on each sample to define the emitting spot.

3. Results and Discussion

Firstly, we discuss the behavior of the slow photoconductivity transients of polycrystalline WO_3 films. After several hours of continuous illumination with white light at room temperature, the conductivity of the sample increased by a few factors relative to the dark value. The photo-Hall measurements were performed to provide separate information concerning carrier concentration and mobility. For polycrystalline WO_3 films, the main contribution to conductivity increase came from the change of carrier concentration.

The relaxation behaviors of photoconductivity can be performed to clarify the energy band and trap levels of oxides. The conductivity of oxide thin films usually slowly decayed at room temperature when illumination was stopped. The time dependence of the photoconductivity $\Delta\sigma$ ($\Delta\sigma = \sigma - \sigma_0$) of WO_3 films followed a simple exponential function as shown in semi-logarithm plots in Fig. 3. Furthermore, the relaxation can be fitted to two exponential decays in two distinct time regions before and after 1×10^4 s. Time constants of 5.0×10^4 and 1.2×10^5 s were obtained, respectively. The double exponential decay indicates two discrete levels participated in the relaxation process. The time required to escape from a trap at energy E_t can be described by the well-known expression [2]:

$$\tau = \frac{1}{\nu}\exp\left(\frac{E_t - E_{ref}}{kT}\right) \quad (1)$$

in which ($E_t - E_{ref}$) is the trap energy relative to either the valance or conduction band (depending on the mechanism), and ν is the attempt-to-escape frequency, which is usually accepted to be the lattice vibration frequency (10^{13} s^{-1}). If we consider that the mechanism is associated with the captured holes, the