SURFACES, INTERFACES, AND THIN FILMS

Effect of Exposure to Optical Radiation and Temperature on the Electrical and Optical Properties of In$_2$O$_3$ Films Produced by Autowave Oxidation

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Submitted March 12, 2013; accepted for publication March 26, 2013

Abstract—Indium-oxide films are synthesized by the autowave-oxidation reaction. It is shown that, upon exposure to optical radiation, the resistance of the films sharply decreases and the maximal relative change in the resistance is 52% at room temperature. Two resistance relaxation rates after termination of the irradiation, 15 Ω s^{-1} during the first 30 s and 7 Ω s^{-1} over the remaining time, are determined. The data of infrared spectroscopy of the films show that exposure to optical radiation induces a 2.4% decrease in the transmittance at a wavelength of 6.3 μm. It is found that, after termination of the irradiation, the transmittance gradually increases with a rate of 0.006% s^{-1}. It is suggested that photoreduction is the dominant mechanism responsible for changes in the electrical and optical properties of the In$_2$O$_3$ films.

1. INTRODUCTION

Indium oxide is a direct wide-gap semiconductor, whose band gap is ~3.7 eV [1]. Thanks to its ability to transmit visible light and conduct current, indium oxide finds wide use in different applications and devices. Thin In$_2$O$_3$ films are used in gas sensors, transparent thin-film transistors, planar displays, electrochromatography devices, solar cells, etc. [2–7]. Indium-oxide films doped with tin are used as constructional materials for space vehicles to lower the level of radiation-induced electrostatic charging [8, 9].

It is known that thin In$_2$O$_3$ films are fabricated by different techniques [2, 10–16] and the physical properties of the films heavily depend on the method of fabrication [2, 11]. At present, low-temperature and simple methods of the production of In$_2$O$_3$ films are being developed [6, 10, 12, 17, 18]. Among these, the technique of the formation of metal-oxide films by combustion at temperatures below 200°C is proposed [10].

Recently, we studied In$_2$O$_3$ films produced by autowave oxidation, which is distinguished by a low initiation temperature (180°C) [19]. The autowave mode of oxidation in thin films is similar to self-propagating high-temperature synthesis (SHS) in powders. The SHS technique was proposed by A.G. Merzhanov, and it is extensively used now for the production of new materials [20]. It is thought that SHS products contain much less impurities compared to the initial mixture

and are high-quality materials [20]. However, the systematic features and dynamics of the propagation of reaction waves in nanofilms are still poorly understood [21].

It was experimentally established that photon treatment in the wavelength range from 750 to 450 nm had an effect on the electrical characteristics of amorphous indium–gallium–zinc oxide transistors [22]. A high rate of recrystallization of thin polycrystalline Au, Pt, and Pd films was observed upon pulsed photon treatment of the films with emission from high-power xenon lamps (in the spectral range 0.2–1.2 μm) [23]. It was experimentally proved that the radiation emitted by a continuous-wave (cw) He–Ne laser at a wavelength of 632.8 nm and by a xenon lamp have a nonthermal effect on In and Sb diffusion on the Si (111) surface [24].

In a number of papers, the effect of exposure to ultraviolet (UV) radiation on the resistance of In$_2$O$_3$ films was shown [25–29]. Upon exposure to UV radiation of In$_2$O$_3$ films, their resistance sharply decreases. After termination of the UV irradiation, the resistance slowly recovers. The quantitative change in the resistance of the In$_2$O$_3$ films when exposed to UV radiation heavily depends on the structure and morphology of the films themselves [25, 27, 29]. The effect of a decrease in the resistance of the films upon exposure to UV radiation can be used to improve the sensitivity

Intensity, arb. units
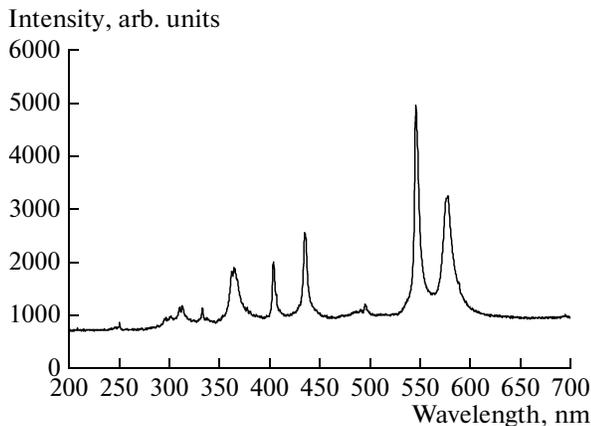
Fig. 1. Emission spectrum of the mercury ultrahigh-pressure gas-discharge lamp used for irradiation of the In_2O_3 films.
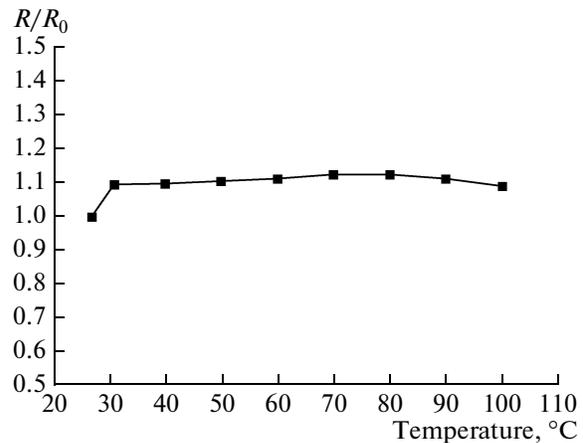
Fig. 2. Temperature dependence of the resistance of the In_2O_3 film without illumination.

of gas sensors produced on the basis of thin In_2O_3 films [26, 29−31]. One of the explanations of this effect is based on the assertion that UV radiation induces the generation of free charge carriers [30].

Of special interest for practical applications are studies of the effect of temperature and optical irradiation on the resistance of In_2O_3 films [32] produced by different techniques.

In this paper, we report the results of studies of the combined effect of temperature and optical irradiation (in the spectral range from 0.2 to 0.7 μm) on the resistance of In_2O_3 films produced by autowave oxidation. We describe the data on relaxation of the resistance and the transmittance in the wavelength range from 5 to 15 μm after irradiation termination.

2. EXPERIMENTAL

The In_2O_3 films to be studied were produced by the autowave-oxidation reaction, which was studied by us previously [19]. The initial $In–In_2O_3$ film was fabricated by the thermal evaporation of pure indium (99.999%) at a pressure of 1.5 Torr in a vacuum chamber. The autowave-oxidation reaction was conducted by heating the initial $In–In_2O_3$ film to a temperature of 200°C at a rate of > 1 K s^{-1}, at a pressure of 0.5 Torr in the vacuum chamber. After the initiation temperature $T_0 \approx 180$°C had been reached, a nucleus of the In_2O_3 phase was formed, and then, being self-sustaining, it spread over the surface. For the substrates, we used cover glass or a p-type silicon wafer chemically cleaned before use. A silicon substrate was used in measurements of the transparency of the films in the infrared (IR) region. The film thickness was measured by X-ray fluorescence analysis and corresponded to ~100 nm.

For the radiation source, we used a 100-W Nikon mercury ultrahigh-pressure gas-discharge lamp. The

radiation spectrum and the power of the lamp were determined with a HR 4000 Ocean Optic spectrometer and a Coherent FieldMax2-to power meter, respectively.

The resistance of the samples was measured by the standard four-probe technique. A Specac thermostat was used in measurements of the resistance of the In_2O_3 films in the temperature range 25−100°C and to maintain a specified temperature during exposure of the sample to light.

A Bruker Vertex 80V spectrometer was used to study the transmittance recovery dynamics in the wavelength range 5−15 μm after termination of exposure to radiation, with subtraction of the spectrum recorded before irradiation. The measurements were carried out in vacuum, at a residual pressure in the chamber of 3×10^{-4} Torr.

3. RESULTS AND DISCUSSION

Figure 1 shows the emission spectrum of the mercury gas-discharge lamp. The emission spectrum exhibits peaks typical of mercury vapor. The power of the lamp was ~0.223 W cm^{-2} at the sample location. From Fig. 2, it can be seen that, in the range 25−100°C, the resistance of the film R varies with temperature only slightly, by ~10% of R_0, where R_0 is the resistance of the In_2O_3 film at room temperature without irradiation.

Figure 3 shows the dependence of the resistance of the In_2O_3 film on the irradiation time and the dynamics of the increase in the resistance after the lamp had been turned off. As the lamp is turned on, the resistance of the film sharply decreases by 52%. This is supposedly due to the generation of free charge carriers and/or due to an increase in the electron mobility because of the desorption of oxygen ions from the interfaces between grains [30].
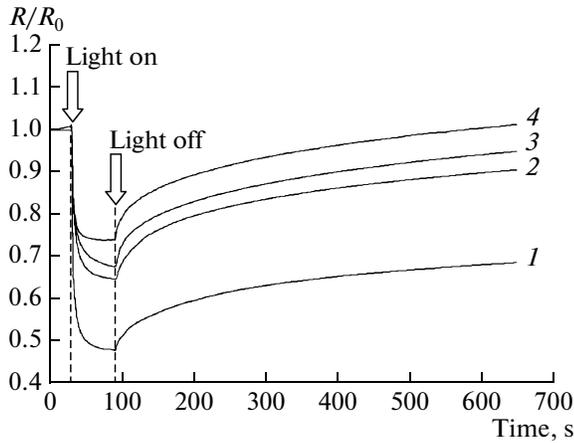
Fig. 3. Time variations in the resistance of the In_2O_3 film upon exposure to optical radiation at substrate temperatures of (*1*) 25, (*2*) 40, (*3*) 80, and (*4*) 100°C.

Fig. 4. Temperature dependence of the resistance of the In_2O_3 film when exposed to optical radiation.

After termination of the irradiation, we observe an increase in the resistance of the In_2O_3 film at a rate of $15\,\Omega\,s^{-1}$ during the first 30 s and $7\,\Omega\,s^{-1}$ after 30 s. The temperature of the sample does not influence the resistance relaxation rate. As the temperature of the In_2O_3 sample is increased, the change in the resistance during irradiation decreases (Fig. 4).

One of the methods for determining the concentration of free charge carriers in semiconductor nanofilms is IR spectroscopy [33]. Within the context of the Drude model for free electrons, the expression that relates the charge-carrier concentration to the plasma absorption frequency ω_p is [34, 35]

$$\omega_p = (Ne^2/m^*\varepsilon_0)^{1/2}.$$

Here, N is the concentration of free charge carriers, e is the elementary charge (1.6×10^{-19} C), $m^* = 0.36m_e$ [36] is the electron effective mass ($m_e = 9.1 \times 10^{-31}$ kg is the free electron mass), and $\varepsilon_0 = 8.85 \times 10^{-12}$ F m^{-1} is the permittivity of free space. In the calculations, we assumed $N = 10^{19}$ cm^{-3}, which corresponds to the resistivity $\sim 2 \times 10^{-2}\,\Omega$ cm [37]. Substituting these data into the above expression, we find that the plasma frequency of the In_2O_3 films produced by autowave oxidation is $\omega_p \approx 3 \times 10^{14}$ s^{-1} (the corresponding wavelength is ~6.3 μm).

We assumed that, in the case of the generation of free charge carriers upon irradiation, absorption would be observed at a frequency close to the plasma frequency. To verify this assumption, we measured the IR transmittance of the In_2O_3 film on the Si substrate after termination of exposure to light (Fig. 5). The transmittance was measured 60 s after termination of irradiation under normal conditions. The delay time of the measurement, 60 s, is chosen with regard to the

time it takes for the Bruker Vertex 80V spectrometer to attain working vacuum.

From Fig. 5, it can be seen that, after termination of the irradiation, the transmittance decreases by 2.4% at a wavelength of 6.3 μm. However, with time, we observe the relaxation process, in which the transmittance gradually increases. From the analysis of transmittance relaxation at the wavelength 6.3 μm, it follows that the rate of increase in the transmittance is $0.006\%\,s^{-1}$.

To correlate the resistance relaxation process with the transmittance relaxation process, we plotted the corresponding experimental data together using one graph (Fig. 6). As can be seen from Fig. 6, the dynamics of the increase in the resistance after irradiation is identical in character to the dynamics of the increase in the transmittance.
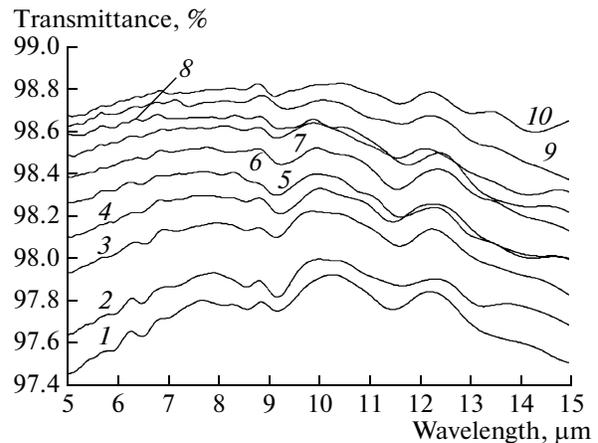
Fig. 5. Transmittance of the In_2O_3 film at room temperature, as measured within (*1*) 60, (*2*) 80, (*3*) 110, (*4*) 130, (*5*) 150, (*6*) 170, (*7*) 190, (*8*) 210, (*9*) 230, and (*10*) 250 s after termination of exposure to optical radiation.
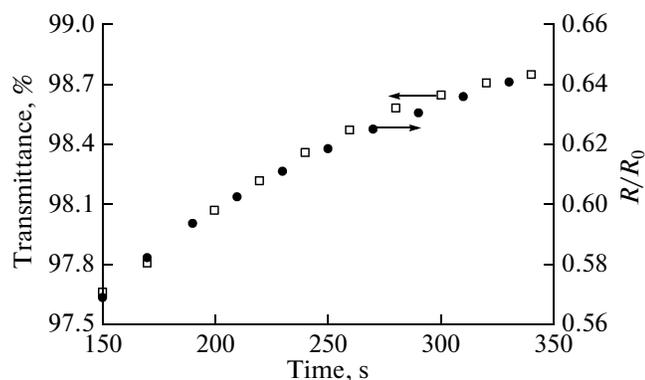
Fig. 6. Relaxation of the resistance and transmittance (at 6.3 μm) of the In_2O_3 film after termination of exposure to optical radiation, as recorded at room temperature.

At present, there exist several concepts of the effect of light on the electrical properties of indium oxide [30]: the effect is attributed to the generation of electron−hole pairs, the desorption of oxygen adsorbates, and optically induced recovery (often referred to as photoreduction). The band gap of In_2O_3 films can lie in the range from 3.5 eV (355 nm) to 4 eV (310 nm), depending on the preparation technique [3]. Therefore, to provide electron transitions from the valence band to the conduction band, it is necessary to expose the In_2O_3 films to light at wavelengths of ≤355 nm. In the emission spectrum of the mercury gas-discharge lamp (see Fig. 1), the emission intensity at wavelengths of ≤355 nm is low and corresponds to the background intensity level. However, a great number of surface defects and interfaces between grains modify the band structure of indium oxide. Consequently, electron transitions can occur also at energies lower than the energy of the band gap [30, 31]. As a result of such transitions, electron−hole pairs can be formed. However, when the lamp is turned off, no sharp step in increasing resistance of the film is observed.

The desorption of oxygen adsorbates from the surface of the conducting transparent oxide films when exposed to light may increase the mobility of charge carriers and, hence, increase the conductivity of the film [38]. In the case under consideration, such an effect of light on the conductivity of the In_2O_3 film is possible, but not dominant. The IR spectroscopy data for the film samples (see Fig. 5) and the similarity of the resistance and transmittance relaxation processes (see Fig. 6) show that the change in the conductivity of the In_2O_3 films is controlled mainly by a change in the electron concentration. Otherwise, the IR spectroscopy data would have to show constant transmittance in the IR region and/or mismatch between the resistance and transmittance relaxation processes.

The mechanism of photoreduction implies that photoexcited holes recombine with bound electrons at In−O chemical bonds. This brings about the breakage of In−O chemical bonds, the release of oxygen atoms, and their migration towards the film surface, where pairs of oxygen atoms form O_2 molecules that can be desorbed from the surface. As a final result, additional oxygen vacancies are formed in the crystal structure, and these vacancies are responsible for the conductivity of the In_2O_3 films [39, 40]. Therefore, we assume that, in the case under consideration, photoreduction is the dominant mechanism of the effect of light on the conductivity of the In_2O_3 films.

The results obtained in this study can be used for the development of In_2O_3-based gas sensors operating at room temperature. With consideration for additional charge carriers and their lifetimes, it is possible to improve the sensitivity of such sensors due to the fact that the gases to be detected are adsorbed at the film surface with the trapping of charge carriers. From the change in the resistance and the resistance relaxation rate, it is possible to determine the type of gas [41, 42].

4. CONCLUSIONS

Indium-oxide films are synthesized on glassy and silicon substrates by the autowave-oxidation reaction. The resistance of the In_2O_3 films changes only slightly (by ~10%) in the temperature range from 25 to 100°C.

It is shown that, upon exposure to light, the resistance of the In_2O_3 films sharply decreases (by 52%). As the temperature is elevated during irradiation, the change in the resistance becomes less pronounced. After termination of irradiation of the film, the resistivity of the film relaxes with two rates, ~15 Ω s^{-1} during the first 30 s and ~7 Ω s^{-1} for the remaining time. The resistance relaxation rate is independent of temperature.

It is established that the transmittance of the films in the wavelength range 5−15 μm decreases after exposure of the sample to light. At the wavelength 6.3 μm, the relative change in the transmittance is 2.4%. It is found that, after termination of the irradiation, the transmittance relaxes with the rate 0.006% s^{-1}.

It is shown that the resistance and transmittance relaxation processes in the In_2O_3 films are similar in character. This result supports the assumption that the generation of additional charge carriers proceeds according to the mechanism of photoreduction.

The results of the study of the effect of optical irradiation on the properties of In_2O_3 films can be used for engineering In_2O_3-based thin-film gas sensors operating at room temperature.

ACKNOWLEDGMENTS

Priority Fields of Development of the Science and Technology Complex of Russia for 2007−2013", state contract no. 14.513.11.0023.

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Translated by E. Smorgonskaya