Pulsed laser deposition of the ion-conducting LiCoO$_2$ films

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Abstract. Pulsed laser deposition on the n-type and p-type sapphire and silicon substrates produced the ion-conducting LiCoO$_2$ films with a thickness of 10 to 100 nm. The films were synthesized from the compound LiCoO$_2$:Li$_2$O targets with the concentrations of Li$_2$O 5% and 10% at the substrate temperature of 25 to 500 °C. The optical and electrical properties and surface morphology of the films obtained were investigated depending on the type of the substrate and the deposition temperature. The surface roughness of the LiCoO$_2$ films weakly depended on the type of substrate and increased from 7 to 35 nm with a decrease in the substrate temperature from 500 to 25 ºС, respectively. The transmission of the LiCoO$_2$ films increased, on the average, by 30% over the entire spectral range under study from 200 to 1000 nm with a change in the substrate temperature from 25 to 500 °C. It has been established that the LiCoO$_2$ films deposited on the silicon substrates exhibit the resistivity of the order of $10^{-7}$ Ω cm for the films prepared on high-conducting n- and p-type silicon, and of the order of $10^{-1}$ Ω cm for those prepared on high-resistance silicon of n-type. The LiCoO$_2$ films deposited on the c-sapphire substrates display dielectric properties.

1 Introduction

A standard electrochromic device has five superimposed layers (a layer of transparent conductive oxide / a cathode electrochromic layer / an ion-conducting layer (electrolyte) / an anode electrochromic layer / a layer of transparent conductive oxide) and is placed in a layered configuration between two laminated substrates [1]. A liquid polymer electrolyte is commonly used as an ion-conducting layer that transmits ions and blocks the current of electrons. The liquid polymer electrolytes have good transport capabilities for H$^+$ and Li$^+$ ions. However, they exert a destructive effect on the adjacent layers of the electrochromic device, which leads to its delamination and shrinkage. In addition, the polymer electrolytes are destroyed at low ambient temperatures [2]. The technologies for producing solid-state thin-film electrolytes from inorganic metal oxides are being developed to create the all-solid-state electrochromic devices [3]. Compared with the laminated devices, the all-solid-state electrochromic devices, even of large area, will be more durable and reliable [4]. The inorganic electrolytes are the ideal candidates for manufacture of the solid-state electrochromic devices without bubble formation and problems of sealing between the adjacent layers. Such electrolytes are highly stable over a wide range of temperatures and are resistant to ultraviolet radiation. One of these candidates is LiCoO$_2$ owing to its electrochemical properties related to intercalation/deintercalation of Li$^+$ ions, which allows it to serve as an excellent supplier and conductor of ions in an all-solid-state electrochromic device. The method for producing LiCoO$_2$ films determines their structural properties and, therefore, their electrochemical activity with ion-conducting properties [5]. The thin LiCoO$_2$ films are obtained by different methods, such as magnetron sputtering.
[6], electrostatic pyrolysis [7], pulsed laser deposition [8], sol-gel method [9], and chemical vapor deposition [10]. The method of pulsed laser deposition is widely used for the formation of thin LiCoO₂ films owing to the minimal deviation in the composition of a solid target and a thin film, in comparison with other physical methods of vapor deposition [8].

Pulsed laser deposition in the drip-free mode makes it possible to obtain the smooth homogeneous films of high quality due to the elimination of the droplets emitted from the target onto the substrate during the film growth [11]. Because of the high energy of particles in laser plasma, the method of pulsed laser deposition reduces the crystallization temperature of films down to room temperature and ensures that the layers of a fully solid-state electrochromic cell are produced on the flexible organic substrates to which high-temperature processes are not applicable. The need to study the dependence of the optical and electrical properties and morphology of the surface of LiCoO₂ films on the temperature and type of the substrate during the growth is associated with the influence of the interface morphology on the diffusion efficiency of lithium ions in electrochromic cells [12]. The investigation of ion-conducting materials is necessary to improve their ionic conductivity and optical transparency [13]. The purpose of this work was to obtain the LiCoO₂ films by the method of pulsed laser deposition in a drip-free mode and to study the optical and electrical properties and surface morphology of the obtained films, depending on the type and temperature of the substrate.

2 Experiment

The method of pulsed laser deposition [14] on the n-type and p-type c-sapphire and silicon substrates permitted the thin LiCoO₂ films to be produced at the substrate temperature from 25 to 500 °C. The thickness of the films obtained varied from 10 to 100 nm. The films were deposited from the compound LiCoO₂:Li₂O targets. The targets were made from the LiCoO₂ and Li₂O powders by pressing and thermal annealing in air at the temperature of 1000 °C for two hours. The concentration of Li₂O in the target was 5% and 10%. The targets were ablated in a vacuum chamber by radiation of an excimer KrF laser with a wavelength of 248 nm at the energy density on the target of at least 2.5 J/cm². The laser radiation was focused by a lens with a focal length of 25 cm at an angle of 45° on the target rotating at the frequency of 1 Hz. The distance between the target and the substrate was 50 mm. In the droplet-free deposition mode, a mechanical separator was placed between the target and the substrate, preventing droplets from falling on the growing film, which made it possible to produce smooth, uniform films of high quality [11]. The vacuum chamber was evacuated using a turbomolecular and cryogenic pumps to a pressure of 10⁻⁷ Torr. The oxygen pressure in the vacuum chamber during the growth was 100 mTorr.

The optical properties of the LiCoO₂ films were investigated on a Cary 50 spectrophotometer. The surface morphology of the films was studied with a Carl Zeiss NVision 40 scanning electron microscope and an NT-MDT Solver Next atomic-force microscope in a semicontact mode. The surface scans were processed using the Nova PX software. The film thickness was determined with the aid of a modified MII-4 (LOMO) microinterferometer. The electrical properties of LiCoO₂ films were studied employing the four-point Van der Paut scheme on an automated HSM 3000 installation.

3 Results and discussion

During the pulsed laser deposition of a thin LiCoO₂ film, the partial oxygen pressure plays an important role, affecting the microstructure and morphology of the film surface; it can also control the variations in the percent composition of the target and the film [5]. Oxygen is supplied to the vacuum chamber in order to compensate for its loss on the surface of the thin oxide film in the course of its growth. During laser ablation of the target, the particles of the laser plume are in the molecular, atomic, and ionic states. With increasing the oxygen pressure, it is possible to attain a deviation from the conditions of molecular beam epitaxy, under which the ablated particles are deposited on the growing film without collisions with the oxygen molecules. With a large buffer gas pressure, the ablated plasma torch particles collide with the oxygen molecules. Lithium, being the lightest element in the periodic table is lighter than cobalt and oxygen; therefore, with a high pressure of molecular
oxygen, it is easily scattered, not reaching the growing film [8]. In this work, we have estimated the free path length \( l \) of the ablated particles of ions and atoms of lithium depending on the partial oxygen pressure \( P \) in the vacuum chamber under the assumption of gas-kinetic cross sections, which is determined by the expression [15]:

\[
l = \frac{1}{Sn},
\]

(1)

where \( S \) is the cross-sectional area of the scattering of ions, atoms or molecules in a collision; \( n \) is the concentration of molecular oxygen particles. Considering that

\[
S = \pi d^2
\]

(2)

where \( d \) is the total diameter of the colliding particles, and the concentration of molecular oxygen particles in cm\(^3\) is expressed through pressure \( p \) in Torr by the formula:

\[
n = \frac{pN_A}{V760}
\]

(3)

where \( p \) is the oxygen pressure, \( V \) is the volume of one mole of gas, \( N_A \) is the Avogadro number, the dependence of the mean free path of the plasma torch particles on the oxygen pressure in the sputtering chamber was calculated from (1). The resulting curves are shown in Fig. 1.

\[Fig. \, 1. \text{ Dependence of the mean free path } l \text{ of ablated ions and lithium atoms on the pressure of molecular oxygen } P_{O2} \text{ in the vacuum chamber: 1 - Li}_2 \, (d = 0.92 \, \text{nm}); \, 2 - \text{Li} \, (d = 0.61 \, \text{nm}); \, 3 - 2\text{Li}^+ \, (d = 0.604 \, \text{nm}); \, 4 - \text{Li}^+ \, (d = 0.452 \, \text{nm}).\]

It can be seen from Fig. 1 that the free path for the ablated torch particles becomes equal to the distance from the target to the substrate, which is 5 cm in our experiments, in the pressure range from 2 \( 10^{-4} \) to 2 \( 10^{-3} \) Torr. However, the films obtained at this pressure of oxygen have poor transmission in the visible region of the spectrum, which does not allow them to be used as an electrolyte of a solid-state electrochromic cell. To improve the efficiency of oxidation of the lithium and cobalt atoms on the surface of the film, a higher pressure of the buffer gas is necessary [8]. In our experiments, the oxygen pressure in the chamber was 100 mTorr. The films were obtained at different temperatures of the sapphire and silicon substrates during their growth. By the AFM method it has been established that a variation in the temperature of the substrate during the growth of a LiCoO\(_2\) film affects the surface roughness. The results of measuring the surface roughness of the LiCoO\(_2\) films obtained at different temperatures of the c-sapphire substrate in the process of their growth are shown in Table 1.

**Table 1. Roughness of LiCoO\(_2\) films deposited on c-sapphire substrates at different temperatures**

| The substrate temperature (°C) | Average roughness (nm) |
|-------------------------------|------------------------|
| 25                            | 33,959 ÷ 34,8          |
| 150                           | 19,207 ÷ 20,403        |
| 500                           | 7,023 ÷ 11,304         |

Table 1 shows that the films grown on the c-sapphire substrates by the method of pulsed laser deposition have a roughness from 7 to 35 nm. The films grown at room temperature have the most developed surface relief; the surface roughness of the film obtained at room temperature of the substrate averages 35 nm. An increase in the substrate temperature during the growth reduces the surface roughness of the lithium cobaltate films by a factor of three. Figure 2 presents the AFM images of the surface of the LiCoO\(_2\) films obtained at 25 °C and 500 °C on the c-sapphire substrates.
Fig. 2. The AFM of the surface of the LiCoO$_2$ film deposited at the temperatures of 25 °C - $a$ and 500 °C - $b$ of the c-sapphire substrate.

Figure 3 shows a SEM image of the surface of the LiCoO$_2$ film on a silicon substrate at room temperature.

Fig. 3. The SEM surfaces of the LiCoO$_2$ film on a silicon substrate, deposited at the substrate temperature of 25 ºC.

The nanostructured surface of the LiCoO$_2$ films is visible both on the AFM and on the SEM images. The size of the granules is several hundred nanometers. The films obtained on the c-sapphire and silicon substrates at room temperature demonstrate the similar surface structure. The results of studying the elemental composition of the surface of the LiCoO$_2$ film on a silicon substrate are presented in Fig. 4.

Fig. 4. The elemental composition of the surface of the LiCoO$_2$ film on a silicon substrate, obtained using SEM.

According to the data of energy dispersive X-ray spectroscopy, the composition of the LiCoO$_2$ films on the silicon substrate corresponded to that of the LiCoO$_2$ target: (10% Li$_2$O).
The investigation of the transmission spectra of the LiCoO$_2$ films obtained on the c-sapphire substrate from the LiCoO$_2$: Li$_2$O targets with the lithium oxide content of 5% showed that when the substrate temperature changes from 25 to 500 °C, the transparency of the films increases by an average of 30% (Fig. 5).

Fig. 5. The transmission of the LiCoO$_2$ films 40 nm thick, obtained on the c-sapphire substrate at a temperature of 25 °C - 1 and 500 °C - 2 in the process of deposition. 3 – the transmission of sapphire.

The resistivity of the LiCoO$_2$ films produced on a c-sapphire substrate also depended on the substrate temperature and increased from 56 Ω·cm to 1 kΩ·cm with a rise of the temperature from 25 to 500 °C.

A peculiarity has been revealed in the behavior of the electrical properties of the LiCoO$_2$ films deposited on the silicon substrates (Table 2). When the concentration of Li$_2$O in the target is 10%, the LiCoO$_2$ films, deposited on the silicon substrates with a specific resistance of $1 \times 10^{-2}$ Ω·cm at room temperature, become highly conductive with a specific resistance of about $2.5 \times 10^{-7}$ Ω·cm.

Table 2. Specific resistance of the LiCoO$_2$ films deposited from the LiCoO$_2$ (10% Li$_2$O) targets on the sapphire and silicon substrates

| Substrate type | Substrate resistivity, Ω·cm | Film thickness, nm | Resistivity, Ω·cm |
|----------------|-----------------------------|-------------------|------------------|
| $c$ - Al$_2$O$_3$ dielectric | 20 | 56 |
| $c$ - Al$_2$O$_3$ dielectric | 24 | 1000 |
| $n$ - type Si | $10^{-4}$ | 18 | $3.7 \times 10^{-4}$ |
| $n$ - type Si | 7 | 41 | $1.2 \times 10^{-1}$ |
| $p$ - type Si | $10^{-3}$ | 30 | $2.5 \times 10^{-7}$ |

A significant increase in the conductivity of the LiCoO$_2$ films may be due to the diffusion of lithium ions into the substrate. This effect is observed for both $n$- and $p$-type silicon substrates. For the highly conductive $n$-type substrates, the effect of an avalanche-like increase in conductivity is more pronounced: an increase by 5 orders of magnitude compared to the $p$-type films, where conductivity has increased by 4 orders of magnitude. This is due to counteracting against the penetration of lithium ions into the silicon on the part of the doping ions in the $p$-silicon substrate. At the same time, the increase in conductivity on the high-resistance $n$-type substrates is much less than on the high-conductive substrates (one order of magnitude compared with five orders for the latter). This may be related to the higher crystalline perfection of the low-alloyed high-resistance silicon substrates. As far as we know, this effect of conductivity increase has not previously been observed.

4 Conclusion

By the method of pulsed laser deposition, the thin ion-conducting LiCoO$_2$ films have been produced on the $n$-type and $p$-type c-sapphire and silicon substrates at different temperatures, from room temperature to 500 °C. The influence of the substrate temperature on the optical transmission and morphology of the obtained films has been studied. The dependence of the film transmission in the range from 200 to 1000 nm on the substrate temperature during the film growth has been established. It has been found by the AFM method that the surface roughness weakly depends on the type of substrate and is 35 nm at room temperature of an s-sapphire substrate. Thus, on varying the substrate...
temperature from 25 to 500 ºC in the course of pulsed laser deposition of films, the transmittance of films can be increased by an average of 30% over the entire spectral range under study, which will create electrochromic cells based on the LiCoO₂ films at room temperature over a wide spectrum range. The effect of increasing the conductivity of the LiCoO₂ films on the n- and p-type silicon substrates has been revealed. It has been established that the LiCoO₂ films deposited on the silicon substrates exhibit the resistivity of the order of 10⁻² Ω cm for the films prepared on high-conducting n- and p-type silicon, and of the order of 10⁻¹ Ω cm for the films prepared on high-resistant n-type silicon. The observed effect appears to be related to the intercalation of lithium ions into the surface layer of silicon. The LiCoO₂ films deposited on the c-sapphire substrates possess dielectric properties.

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