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$LiCoO_2$ thin films for gas sensing application

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ABSTRACT

The layered transition metal oxide compounds which are composed of hexagonal close packed oxygen atoms network with lithium and transition metal ions in an alternating (111) planes, such as $LiCoO_2$, $LiNiO_2$, $LiCo_xNi_{1-x}O_2$ etc. have been studied extensively as alternate cathode materials for low power applications. $LiCoO_2$ thin films have been widely considered as good candidates for their use as environmental gas sensors for detecting pollutant gases like carbon monoxide, carbon dioxide, hydrocarbons, ammonia and nitrogen oxides. The device performance is related to the structural properties and morphological features of the film, which in turn dependant on the deposition technique as well as the preparative parameters. Hence in the present investigation $LiCoO_2$ thin films were prepared by pulsed laser deposition and the gas sensing properties of $LiCoO_2$ thin films were studied. When the reducing gas is exposed to the sensing element, it reduces the resistance of the material, which confirms the typical characteristic of a n-type material.

KEYWORDS

$LiCoO_2$;
Thin films;
Pulsed laser deposition;
Gas sensor.

INTRODUCTION

Advances in science and engineering related to the emerging technologies of lithium-ion batteries have been so spectacular in the past decade that they have become the most popular power source for portable computing, battery cars, microelectronics, biomedical implantable devices and telecommunication[1]. Recently, thin films of functional materials including oxide ceramics have become important for use in many electronic, photonic, magnetic, ionic, etc., devices. Most of them have been fabricated through the so-called highly technical processing routes that require a high consumption of energy. However, we must consider also total environmental load of these processing in addition to their capability. There is a growing interest in thin film batteries with smaller dimension. The cathode is one of the critical components of a lithium-ion battery and it determines the capacity, cyclic performance and thermal stability of the battery. The layered transition metal oxide compounds which are composed of hexagonal close packed oxygen atoms network with lithium and transition metal ions in an alternating (111) planes, such as $LiCoO_2$, $LiNiO_2$, $LiCo_xNi_{1-x}O_2$ etc. have been studied extensively as alternate cathode materials for low power applications. Among them, $LiCoO_2$ has found large scale potential applications in the commercial lithium ion batteries. Also it has been widely used as cathode material due to advantages of high specific capacity, high operating voltage, good reversibility, low self-discharge and long cycle life. For the cathode materials, $LiCoO_2$ is extensively studied and applied. The reason for this success is that Li^+ ions can be deintercalated from $LiCoO_2$ down to $Li_{0.5}CoO_2$ with a very good reversibility and a high electrochemical potential, giving rise to batteries with a good cyclability and a high voltage[2].

Recently, a number of new approaches for the preparation of $LiCoO_2$ with improved properties have been developed. $LiCoO_2$ thin films can be obtained by various techniques such as radio frequency (rf) sputtering[3], pulsed laser deposition (PLD)[4-6], electrostatic spray deposition[7] and chemical vapour deposition[8]. Many efforts have been devoted to investigate the crystal structure and electrochemical properties of $LiCoO_2$. Even though the technology is rather expensive and the material is highly toxic, lithium cobaltate is still the most widely used cathode material in lithium-ion batteries. PLD has been widely recognized as a very promising, versatile and efficient method for the deposition of metal oxide thin films[9]. PLD is a powerful and flexible technique for fabricating simple and complex metal oxide films, and has several advantages for thin film deposition: (1) Direct stoichiometry transfer from the target to the growing film (2) High deposition rate and inherent simplicity for the growth of multilayered structures and (3) Dense, textured films can be produced more easily by PLD with in situ substrate heating. In thin film deposition, the substrate temperature plays the important role of determining the thermo emf of films. In this study, we have deposited $LiCoO_2$ thin films on silicon substrates and investigated the thermodynamic properties of these thin films.

EXPERIMENTAL

$LiCoO_2$ thin films were prepared by pulsed laser deposition technique. $LiCoO_2$ target was prepared by sintering a mixture of high purity $LiCoO_2$ powders (Cerac products) by adding Li_2O. The mixture was crushed and pressed at 5 tonns.cm^{-2} to make tablets of 3 mm thick and 13 mm diameter. To get quite robust targets, the tablets were sintered in air at 800 ^{0}C. The typical substrates i.e. Si wafers were cleaned using HF solution. The target was rotated at 10 rotations per minute with an electric motor to avoid depletion of material at any given spot. The laser used in these experiments is the 248 nm line of a KrF excimer laser (Luminics PM 882) with 10 ns pulse with a repetition rate of 10 Hz. The rectangular spot size of the laser pulse was 1 x 3 mm^2 and the energy 300 mJ. The target substrate distance was 4 cm. The deposition temperature was maintained with thermocouple and temperature controller. During the deposition pure oxygen was introduced into the deposition chamber and desired pressure was maintained with a flow controller[10].

RESULTS AND DISCUSSION

The deposition parameters such as substrate temperature, deposition rate, film – substrate combination, vacuum during the film deposition etc. greatly influence the physical and chemical properties of the oxide thin films. In the present investigation thin films of $LiCoO_2$ were prepared on Si substrates keeping all the deposition parameters fixed except the substrate temperature. The electrical conductance of a semiconducting oxide-based gas sensor depends on the chemisorbed oxygen ions, oxygen vacancies and the interstitial ions. The target gases change the oxygen balance of the oxide sensor, leading to a variation in its conductance. It is believed that in most of semiconducting oxide-based devices, the electrical conductance of a semiconducting oxide-based gas sensor depends on the chemisorbed oxygen ions, oxygen vacancies and the interstitial ions. The target gases change the oxygen balance of the oxide sensor, leading to a variation in its conductance.

The conductance of the sensor in dry air was measured by means of conventional circuitary by applying constant voltage and measuring the current by picoammeter. The conductance was measured both in the presence and absence of test gas. The gas response (S) is defined as the ratio of change in conductance in gas to air to the original conductance in air

$$S = (G_g - G_a) / G_a$$

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$LiCoO_2$ conductometric sensors were mounted on an electric heater. Gas response measurements of the devices were performed in a stainless steel test chamber made from Teflon, which was sealed in a quartz lid. The heater was controlled by a regulated DC power supply providing different operating temperatures. The total flow rate was kept constant at 100 sccm and dry synthetic air was used as the reference gas. Subsequently, the device was exposed to sequences of different concentrations of NO_2 for several hours. In the $LiCoO_2$ sensor, change in the oxygen balance of the oxide layer leads to a variation in its conductance. In the case of an oxidizing gas (NO_2), reactions directly take place on the oxide surface.

$LiCoO_2$ films were exposed to different concentrations of NO_2 gas at various temperatures. The sensor was placed in a stainless steel test chamber. A continuous flow of gas (100 sccm) passes through the chamber, which makes the pressure in the test chamber to be nearly atmospheric. The desired gas concentration is obtained by mixing the appropriate flows of gases by means of mass flow controllers. The films are generally heat treated before exposure to different gasses because it produces contacts between grains, many of which are between grains having different crystal structures. When both the films are exposed to NO_2 gas, the dc electrical resistance of the film dramatically increased. Since $LiCoO_2$ is an n type semiconductor, its electrical behavior upon exposure of NO_2 oxidizing gas can be explained by a decrease of conduction carrier density. The amount of oxygen ions available on the $LiCoO_2$ surface increases at the operating temperature. The adsorbing NO_2 molecules interact directly with the adsorption sites at the oxide surface. Therefore the interaction between the film and NO_2 is as follows;

$$NO_2 + e^- \rightarrow NO^{2-} (ad)$$

The interaction with NO_2 results in a decrease in the free electron concentration. The decrease in free carrier concentration causes a rise in the film resistance. The sensitivity of the prepared $LiCoO_2$ thin films for various gas concentrations can be calculated from the equation defined as follows:

$$S = R_a/R_g$$

where S is the sensitivity, R_a is the resistance of a sensor in air medium and R_g is the resistance of a sensor in a test gas medium. The calculations were made by taking the resistance values at the time after which there was no significant decrease in the resistance. The results of the sensing experiments were graphically presented in Figure 1. When the reducing gas is exposed to the sensing element, it reduces the resistance of the material, which confirms the typical characteristic of a n-type material. It is clearly observed that, as the test gas concentration was increased the resistance decreased drastically.

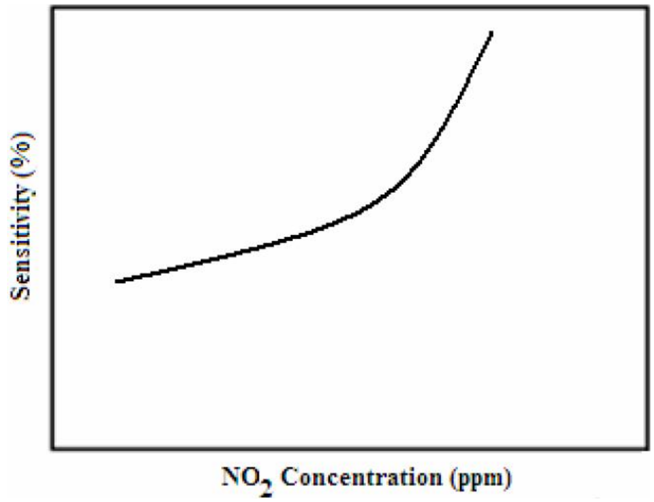

Figure 1 : NO_2 concentration as a function of sensitivity

CONCLUSIONS

Gas sensors based on metal oxide semiconductors may be used in a wide variety of applications including gas monitoring and alarm applications. As some other transition metal oxides, $LiCoO_2$ shows good adsorption of ammonia, carbon oxide, nitric oxides and hydrogen. It is also sensitive to many organic compounds such as hydro carbonic and aromatic gases, ethanol, gasoline, trimethylamine and many others. Chemical sensors that are small, portable, cost efficient and able to detect low concentrations of gases are needed for this application. $LiCoO_2$ films were exposed to different concentrations of NO_2 gas at various temperatures and the sensitivities of the films were recorded at various temperatures. If a sensor exhibits a specialized response to one gas only, then it can be used to detect that gas since there will be no interference by other gases. The ultimate goal is to create a useful chemical gas sensor that can be used to determine the concentration of one gas in air at the lowest concentration possible before it becomes dangerous to human health.

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