THERMODYNAMIC EVALUATION OF ADSORPTION OF ZINC COMPLEX AND ZnO NANO-LAYER PREPARED BY TSCD METHOD BASED ON LANGMUIR ADSORPTION MODEL

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Abstract   Zinc oxide thin films were deposited on soda-lime glass substrates from an aqueous zinc-containing complex by two-stage chemical deposition (TSCD) method. Longmuir adsorption model showed that the adsorption of atoms on the surface of the substrate was typically physical. The relation between the fractional coverage, θ, with the equilibrium constant of the adsorption reaction was nonlinear indicating that the adsorption was non-ideal. The percentage of porosity, $1-\theta$, of the thin layer was determined as a function of Zn^{2+} concentration of the solution. By application of XRD technique, it was shown that pure crystalline ZnO of controllable thickness could be deposited by TSCD method on the surface of the substrate. The procedure consisted of immersion into (a) cold Zn^{2+} complex containing solution and (b) hot water at 90, 95 and 98˚C.

Keywords   Zinc Oxide, Langmuir Adsorption, Physisorption, Immersion, TSCD

چکیده   در این مقاله، لایه های نازک روی اکسید روی توسط رسوب شیمیایی دو مرحله ای (TSCD) با استفاده از یک محلول کمپلکس حاوی فلز روی بر سطح زیر لایه های شیشه سودالایم رسوب داده شدند. مدل جذب لانگمویر نشان داد که جذب اتم ها روی سطح زیر لایه از نوع فیزیکی بوده و ارتباط بین کسر پوشش (θ) با ثابت تعادل واکنش جذب، غیرخطی می‌باشد. این امر نشان داد که فرایند جذب غیرایده‌آل است. درصد تخلخل (θ-1) لایه نازک به‌صورت تابعی از غلظت یون‌های روی در محلول تعیین شد. با استفاده از تکنیک XRD، نشان داده شد که اکسید روی خالص کریستالی با ضخامتی قابل کنترل می‌تواند توسط روش TSCD روی سطح زیر لایه راسب شود. فرآیند رسوب کردن مشتمل بر غوطه‌وری در (الف) محلول کمپلکس سرد حاوی یون‌های روی و (ب) آب داغ در دماهای ۹۰، ۹۵ و ۹۸ درجه سانتی‌گراد می‌باشد.

1. INTRODUCTION

Two-stage chemical deposition (TSCD) consists of immersion into cold ZnO-ammonia solution and then into hot water of a smooth substrate. The procedure is usually repeated to achieve a thicker layer. The film has a low electrical conductivity. But it can be altered. Doping with $SnCl_2$ or annealing after immersion can change the electrical conductivity of the layer [1-3]. The method has proved both non-toxic and feasible [4,5]. It is, therefore, practically attractive to industrialists.

Atoms laying on a surface of liquid or solid exert attractive forces to the adjacent phases. Since the disorder decreases with the surface adsorption of an atom, the entropy change is usually negative for an adsorption reaction to occur. It is therefore necessary for an adsorption reaction to be

exothermic to satisfy its spontaneity. Two types of surface adsorption can be recognized on the basis of the values of the energies exchanged. Physisorption proceeds with small physical force and small energy of activation. In chemisorption, the formation of more than one atomic layer on the solid surface is not possible. Physisorption can be performed at low temperatures to adsorb different atomic layers on the solid surface of the substrate. Because of weak interactions, physisorption has no effect on chemical reactions. Measurement of area of the surface porosity can help determination of the type of adsorption. Like distillation process, physisorption can be applied to different surfaces. Degree of physisorption is considerable under the boiling temperature [6-8].

The amounts of the surface adsorption are evaluated here. Langmuir adsorption criterion is used to decide on ideality or non-ideality of the process. Oxide species adsorbed on the surface of the substrate has been characterized for the first time in this investigation.

2. EXPERIMENTAL PROCEDURE

The starting materials, $ZnCl_2$ and ammonia, were purchased from Merck and were used without further purification.

Soda-lime glass plates (25×15×1 mm, Cat. No. 7101, China) were used as solid substrate for thin film growth. After degreasing with soap solution, the plates were washed with deionized water and dried in a stream of hot air. Aqueous solutions containing $(NH_4)_2ZnO_2$ were prepared by mixing concentrated ammonia with appropriate amount of $ZnCl_2$ until white $Zn\,(OH)_2$ was precipitated. Further addition of ammonia resulted in dissolving of the precipitate. The solution was diluted up to 0.05, 0.1, 0.2 and 0.3 M concentration of Zn^{2+} complex. A cleaned glass substrate was first immersed into a cold (15˚C) complex-containing solution and then in hot water (90-100˚C).

Image analyzer was used to obtain the percentage of porosity of the film. Crystalline structure of the film was determined by XRD technique. XRD diffractograms were obtained using CuKα radiation beams produced by a Philips PW1390 apparatus. The Fourier transform infrared (FTIR) absorption spectra were collected for the prepared sample using FTIR spectrometer (VECTOR33, BRUKER). Also, NaCl solution was used to perform FTIR measurements.

3. RESULTS AND DISCUSSION

Based on the following assumptions, the rate of surface adsorption can be determined from the aid of the Langmuir isotherm:

(a)   Adsorption process is only carried out on the specific sites on the surface
(b)   Each surface site adsorbs one particle
(c)   Surface coverage is monolayer
(d)   Because of adsorption at special sites, adsorbed molecules possess localized concentration
(e)   The distribution of energy on the surface is uniform
(f)   There is no interaction among the adsorbed species
(g)   Large molecules may occupy more than one adsorption site.

In order to evaluate the nature and the type of complex, FTIR measurements was performed. Infrared spectrum is an important record, which provides information about the structure of a compound. In this technique, almost all functional groups in a molecule characteristically absorb a definite range of frequency [9]. Transmission of FTIR radiation causes various molecule bonds to stretch and bend with respect to one another. In this research work, the complex powder was prepared by evaporating the complex solution, spontaneously and the remaining powder-like materials analyzed by Fourier transform infrared spectroscopy. Infrared transmission spectrum of the complex powder obtained in this way is recorded to be in the range of 400-4000 cm⁻¹. The result is shown in Figure 1.

The aim of the present FTIR spectral analysis on the complex powder includes, confirming the complex formation, in addition to proving the absence of any unwished materials in the complex powder. The systematic interpretation of the FTIR spectrum can be of great help to determine whether
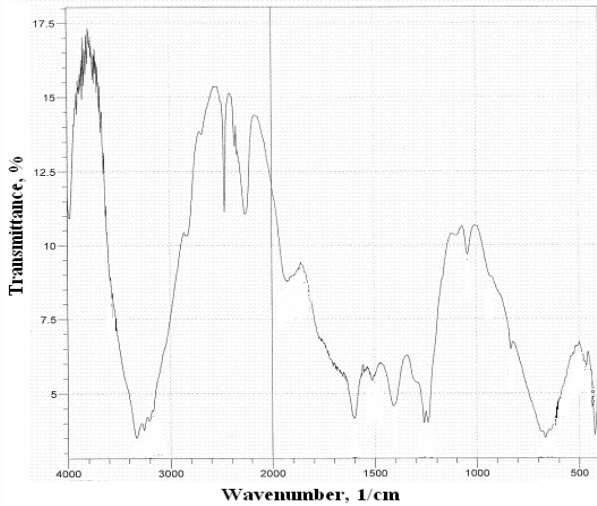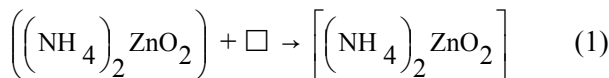
Figure 1. FTIR spectrum of complex powder.

a reaction has occurred to give the predicted product or not, since there may be a possibility of other reaction having occurred. The absorption region from 650 to 1500 cm^{-1} generally represents the finger print region of those materials which are unique in characteristics. As reported in the literature [10], Zn-H vibrations (both symmetric and asymmetric) are indexed around 1500 cm^{-1} and N-H is observed around 3200 cm^{-1} [3,6,7,9]. The presence of Zn-H vibration may be attributed to the adsorption of hydrogen during the evaporation of the complex solution. Therefore it is concluded that the adsorped material on the substrate can be assumed as $(NH_4)_2ZnO_2$.

The adsorption of zinc complex layer and oxide species produced from the decomposition of the complex on the surface of the substrate can be demonstrated by Equations 1 and 2:

$$\left(\left(NH_4\right)_2ZnO_2\right) + \square \rightarrow \left[\left(NH_4\right)_2ZnO_2\right] \qquad (1)$$

$$\left(ZnO\right) + \square \rightarrow \left[ZnO\right] \qquad (2)$$

The signs ( ), [ ] and $\square$ represent adsorbed molecule, occupied site and unoccupied sites (un-s), respectively. Assuming that the rate of adsorption is proportional to both the number of incident molecules (concentration of complex containing zinc ions) and the number of vacant sites available

on the surface, the rate of surface adsorption can be determined from:

$$\left(\frac{d\theta}{dt}\right)_1 = k_f \cdot C_A \left(1-\theta\right) \qquad (3)$$

In which θ is the fraction of the occupied sites, subscript f stands for the forward direction, k_f is the rate constant of the forward process and C_A is the concentration of the adsorbed material.

Because the decomposition reaction of complex containing Zn^{2+} to zinc oxide is unidirectional and the desorption rate of oxide particles, $\left(\frac{d\theta}{dt}\right)_2$, is very low, it is concluded that the above-mentioned reaction is unidirectional and $\left(\frac{d\theta}{dt}\right)_2$ is negligible. Therefore the net rate of adsorption is:

$$\frac{d\theta}{dt} = k_f C_A \left(1-\theta\right) \qquad (4)$$

To determine whether the adsorbed oxide particles act as Ideal adsorbed material, it can be used from the measurements of layer porosity, $1-\theta$, at different concentrations of complex solution. The equilibrium constant of the reaction can be related to the fractional coverage and the fractional unoccupied sites. According to Equations 1 and 2, the equilibrium constants can be calculated as:

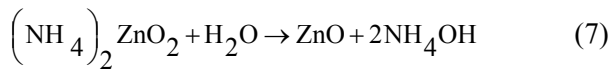$$K_1 = \frac{a\left[\left(NH_4\right)_2ZnO_2\right]}{a\left(\left(NH_4\right)_2ZnO_2\right) \cdot a_{un-s}} = \frac{\gamma_1 \cdot \theta}{\gamma_2 \cdot C_{complex} \cdot \left(1-\theta\right)} = \frac{\gamma\theta}{C_{complex} \cdot \left(1-\theta\right)} \qquad (5)$$

$$K_2 = \frac{a\left[ZnO\right]}{a\left(ZnO\right) \cdot a_{un-s}} = \frac{\gamma'_1 \cdot \theta}{\gamma'_2 \cdot dC_{Zn^{2+}} \cdot \left(1-\theta\right)} = \frac{\gamma'\theta}{dC_{Zn^{2+}} \left(1-\theta\right)} \qquad (6)$$

Where d is the decomposition percent of complex to zinc oxide and its value is less than unit. In order to determine d, consider the reaction of

decomposition of complex to ZnO as follows:

$$\left(NH_4\right)_2 ZnO_2 + H_2O \rightarrow ZnO + 2NH_4OH \qquad (7)$$

The theoretical weight of zinc oxide, $m_{th.}$ can be determined by knowing the weight of complex deposited on the surface of substrate, m.

$$m_{th.} = \frac{m.M}{M'} \qquad (8)$$

In which M and M′ are the molecular weight of zinc oxide and complex, $(NH_4)_2 ZnO_2$, respectively.

The average of d can be obtained from the comparison of the weight of zinc oxide determined experimentally, m_{ex}, at various times. The values of $m_{th.}$ and m_{ex} are given in Table 1.

Therefore it is concluded that:

$$C_{ZnO} = 0.9084\, C_{Zn}{}^{2+}$$

Equations 5 and 6 can be rewritten as:

$$\frac{\theta}{1-\theta} = \frac{k_1}{\gamma} C_{complex} \qquad (9)$$

$$\frac{\theta}{1-\theta} = \frac{k_2}{\gamma'} dC_{zn^{2+}} \qquad (10)$$

If the adsorbed material act as an ideal species, its activity coefficient is unit and therefore, $\frac{k_1}{\gamma}$ and $\frac{k_2}{\gamma'}$ are constant.

The percent of porosity of complex and oxide layers at various concentrations of aqueous solution are given in Tables 2 and 3. Also, the values of $\frac{\theta}{1-\theta}$, $\frac{k_1}{\gamma}$ and $\frac{k_2}{\gamma'}$ are given in Tables 2 and 3. As it is shown, $\frac{k_1}{\gamma}$ and $\frac{k_2}{\gamma'}$ are not constant

TABLE 1. The Values of $m_{th.}$, $m_{ex.}$ and Average of d.

Dipping Time (s.)	m_{th}	m_{ex}	$\left\|\frac{m_{ex.} - m_{tn.}}{m_{tn.}}\right\| \times 100$	$\bar{d}$
1	9.27×10^{-3}	5×10^{-4}	94.6062	
2	6.95×10^{-3}	7×10^{-4}	89.928	
5	5.9×10^{-3}	9×10^{-4}	84.77	90.84 % = 0.9084
8	0.0119	1.2×10^{-3}	89.916	
12	0.0259	1.3×10^{-3}	94.9806	

TABLE 2. The Percentage of Porosity, $\frac{\theta}{1-\theta}$ and $\frac{k_1}{\gamma}$ Related in the

Process of Adsorption of the Complex on the Surface.

Concentration (M)	% Porosity , $(1-\theta)$	θ	$\frac{\theta}{1-\theta}$	$\frac{k_1}{\gamma}$
0.05	0.82	0.18	0.2195	4.39
0.1	0.75	0.15	0.2	2
0.2	0.67	0.33	0.4925	2.4625
0.3	0.60	0.40	0.666	2.22

and it is concluded that the adsorped material is non- ideal. It is necessary to note that even if $\frac{k_1}{\gamma}$ and $\frac{k_2}{\gamma'}$ are constant, it is possible the adsorped materials have a non- ideal behavior.

The dependence of $\frac{\theta}{1-\theta}$ versus the concentration in the adsorption of the complex and oxide layer respectively is given by:

$$\frac{\theta}{1-\theta} = 0.48 \, C_{complex} - 0.027$$

$$\frac{\theta}{1-\theta} = -0.78 \, d \, C_{Zn}^{2+} + 0.68 \qquad (11)$$

According to Equation 11 the percent of porosity and the occupied surface sites can be theoretically calculated at the various concentrations of aqueous solution.

With regards to the phase present and texture, XRD pattern for oxide deposits grown on soda-lime glass is shown in Figure 2. In this X-ray diffraction spectrum, the peaks at 2 Theta = 31.3, 34.6, 36.2, and 72.6 corresponding to the planes (100), (002), (101), and (004) respectively, of the hexagonal phase of ZnO, zincite, were present. The peak at 2 Theta = 34.6, which corresponds to the diffraction from the (002) plane, was very strong. This film exhibited a preferential orientation with the c axis perpendicular to the substrate. The same preferred orientation of the films was found in the case of ZnO films prepared using other methods [11-13].

TABLE 3. The Percentage of Porosity, $\dfrac{\theta}{1-\theta}$ and $\dfrac{k_2}{\gamma'}$ Related in the Process of Adsorption of Oxide Layer on the Surface.

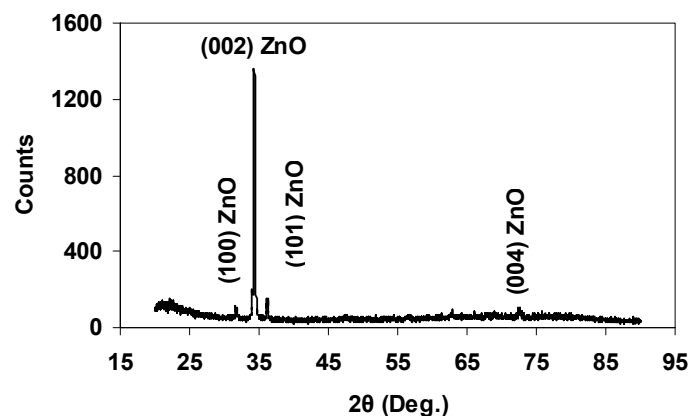| Concentration (M)	% porosity , $(1-\theta)$	θ	$\dfrac{\theta}{1-\theta}$	$\dfrac{k_2}{\gamma'}$
0.05	0.6	0.4	0.666	14.66
0.1	0.63	0.37	0.5873	6.465
0.2	0.65	0.35	0.5385	2.964
0.3	0.68	0.32	0.4706	1.727

Figure 2. XRD patterns for ZnO deposits on soda-lime glass substrate annealed at 180˚C.

4. CONCLUSION

Pure ZnO thin films can easily be deposited by successive immersion of soda-lime substrate into a cold ammonia complex containing solution and then into hot water. Varying the number of successive dipping-growing stages, one can control the thickness of the film. This film exhibited a preferential orientation with the c axis perpendicular to the substrate. According to the Longmuir model and also the measurement of the percent of porosity of complex and oxide layers at various concentrations of aqueous solution, the adsorped materials including the complex and zinc oxide thin film have non-ideal behavior. Also, the percent of porosity and the occupied surface sites can be theoretically calculated at the various concentrations of aqueous solution.

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