ISSN 0023-1584, Kinetics and Catalysis, 2007, Vol. 48, No. 5, pp. 636–639. © MAIK “Nauka/Interperiodica” (Russia), 2007.
Original Russian Text © V.G. Parvanyan, F.A. Grigoryan, E.R. Arakelova, G.G. Asatryan, G.N. Mirzoyan, G.G. Petrosyan, 2007, published in Kinetika i Kataliz, 2007, Vol. 48, No. 5, pp. 681–684.

Formation and Decomposition of a Volatile Zn-Containing Complex for the Synthesis of ZnO Films

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Received June 22, 2006

Abstract—The formation of a Zn-containing complex on a ZnO target in an H_2O_2 vapor medium, the sublimation of this complex, and the decomposition of the complex to the original compound are considered. UV preirradiation of the target raises the concentration of the Zn-containing complex in the gas phase in proportion to the irradiation time. The rate constant of the decomposition of the complex on a substrate is reported. The activation energy and the preexponential factor (k_0) for the decomposition reaction are derived from the temperature dependence of the rate constant. The fact that the activation energy of the decomposition of the complex is similar to that of hydrogen peroxide decomposition suggests that the complex has a peroxide-like structure. The experimental and calculated k_0 data indicate that the decomposition reaction is monomolecular.

DOI: 10.1134/S0023158407050060

Semiconducting ZnO films are widely used in various optoelectronic and sensor devices [1–3]. The energy released in H_2O_2 adsorption onto oxide surfaces is sometimes sufficient for the formation of free radicals [4, 5] and electronically excited states in the solid [5, 6].

It was demonstrated that hydrogen peroxide decomposition on the zinc oxide surface is accompanied by the formation of a Zn-containing complex [7, 8]. This complex can pass into the gas phase and decompose on a solid substrate to yield the starting compound, ZnO. This is an example of a chemical transport reaction. Various transport reactions have found wide application in science and engineering. As an efficient means of matter transport, they play a significant role in the deposition of films and coatings.

Here, we report the formation of a volatile Zn-containing complex on a ZnO target, the decomposition of this complex on a substrate, and the effect of the UV irradiation of the target on the complex concentration in the gas phase.

EXPERIMENTAL

The formation and decomposition of the Zn-containing complex were studied in a vacuum quartz flow reactor (Fig. 1) at low pressures.

Hydrogen peroxide vapor (98%) at 5–25 Pa was fed into the reactor containing a polycrystalline ZnO target as a tablet prepared by double-side dry pressing at 400–1500 kgf/cm^2.

The substrates were five quartz cylinders (d = 1.4 cm, l = 1.4 cm) placed in series 1 cm from the target and 200 cm from a liquid-nitrogen trap. The substrate temperature was 293–423 K, and the target temperature was 373 K.

Experiments demonstrated that the Zn-containing complex is stable in the gas phase and undergoes heterogeneous decomposition on the solid surface. The process taking place in the reaction zone can be viewed as consisting of the following two steps: the formation of a Zn-containing complex, which then passes into the gas phase, and the decomposition of the complex on the substrate, resulting in a zinc oxide film.

The formation and accumulation kinetics of the Zn-containing complex in the reaction zone are determined by the interplay of two competing processes, namely, the generation of the complex on the target surface, followed by the transfer of the complex to the gas

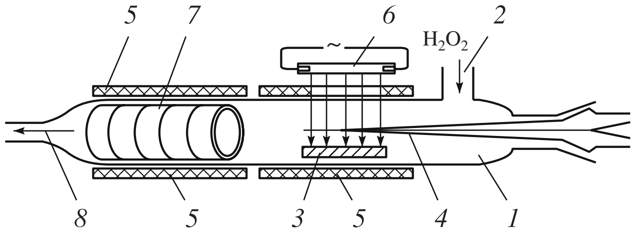

Fig. 1. Schematic of the quartz flow reactor: (*1*) quartz tube, (*2*) H_2O_2 vapor inlet, (*3*) ZnO target, (*4*) thermocouple, (*5*) resistance furnaces, (*6*) mercury lamp, (*7*) quartz substrates, and (*8*) H_2O_2 vapor outlet.

phase, and the decomposition of the complex on the ZnO target and reactor surfaces.

Under the assumption that the decomposition of the complex on the target and reactor surfaces is a first-order reaction and the formation rate of the complex is independent of the contact time, the variation of the complex concentration in the gas phase can be described by the equation

$$[\mathrm{N}] = [\mathrm{N}]_0(1 - e^{-k_{\mathrm{het}}t}), \qquad (1)$$

where [N] is the complex concentration in the gas phase as a function of the contact time, $[\mathrm{N}]_0$ is the maximum concentration of the complex (which is reached at a long contact time), k_{het} is the rate constant of the heterogeneous decomposition of the complex on the target and reactor surfaces, and t is the contact time.

The concentration of the Zn-containing complex in the gas phase was calculated using the familiar expression

$$[\mathrm{N}] = 0.975\frac{10^{19}}{T}Pf, \qquad (2)$$

where [N] is the concentration of the Zn-containing complex (particle/cm^3) in the gas phase near a given substrate, P is pressure (Torr), T is the target temperature (K), $f = \frac{\sum m_{\mathrm{Zn}^{2+}}}{\sum m_{\mathrm{tot}}}$ is the mole fraction of the Zn-containing complex in the gas phase near the substrate, $\sum m_{\mathrm{tot}}$ is total amount of H_2O_2 and H_2O (mol) introduced into the gas phase, and $\sum m_{\mathrm{Zn}^{2+}}$ is the amount of the Zn-containing complex (mol) in the gas phase. The Zn-containing complex decomposed on the substrates, in the trap, and on the reactor walls.

The consumption of ZnO on the target is equal to the amount of the complex decomposed on the substrates, in the trap, and on the reactor walls. The amount of ZnO deposited on the substrates, in the trap, and on the reactor walls was determined by atomic absorption spectrometry. The concentration of the Zn-containing complex in the gas phase was governed by the amount of ZnO deposited.

The amount of the Zn-containing complex in the gas phase near a given substrate ($\sum \nu_{\mathrm{Zn}^{2+}}$) was calculated as the total amount of the complex decomposed on the substrates, in the trap, and on the reactor walls minus the amount of the complex decomposed upstream of the given substrate.

Equation (1) can be rewritten as

$$\ln\frac{[\mathrm{N}]_0}{[\mathrm{N}]_0 - [\mathrm{N}]} = k_{\mathrm{het}}t. \qquad (3)$$

Equation (3) was used to derive the rate constant of the heterogeneous decomposition of the complex from calculated values of the maximum complex concentration ($[\mathrm{N}]_0$) and of complex concentrations at various flow rates ([N]).

The linearity of $\ln\frac{[\mathrm{N}]_0}{[\mathrm{N}]_0 - [\mathrm{N}]}$ as a function of t would be evidence that the experimental data are in agreement with the data calculated using Eqs. (1) and (3).

In order to increase the complex generation efficiency, the ZnO target surface was preirradiated with UV light from a DRSh-250W mercury lamp (exposure time, 2–7 h), and the data obtained after irradiation were compared to the data obtained without irradiation.

The volumetric flow rate was maintained constant in each run and was determined from the consumption of H_2O_2 and H_2O by weighing the evaporator before and after the run. Therefore, the rate of the Zn-containing complex inflow into the substrate zone was invariable within one run.

Under the assumption that the decomposition of the complex on the substrates is a first-order reaction, the complex concentration as a function of the contact time can be expressed as

$$\ln[\mathrm{N}] = \ln[\mathrm{N}]_0 - k_n t, \qquad (4)$$

where $[\mathrm{N}]_0$ and [N] are the concentrations of the complex in the gas phase (particle/cm^3) at the entrance of the substrate zone and near the substrate for which the contact time is considered and k_n is the rate constant of the heterogeneous decomposition of the complex on the substrate (s^{-1}).

The applicability condition for Eqs. (1), (3), and (4) is given by the following inequality [9]:

$$\frac{kD}{V^2} \ll 1, \qquad (5)$$

where D is the diffusion coefficient of the complex and V is the linear flow velocity.

The rate constant of the heterogeneous decomposition of the complex was determined by measuring the complex concentration near a substrate as a function of the contact time.

RESULTS AND DISCUSSION

Formation of the Zn-Containing Complex

Figure 2 plots the concentration of the Zn-containing complex on the target as a function of the contact time for the unirradiated target and for the target exposed to UV light for 7 h. As was expected, at long contact times, the complex concentration tends to its constant maximum value $[\mathrm{N}]_0$ in all runs. The $[\mathrm{N}]_0$ value for the UV-preirradiated ZnO target is one order of magnitude larger than the same value for the unirradiated target. As is clear from Fig. 2, the maximum

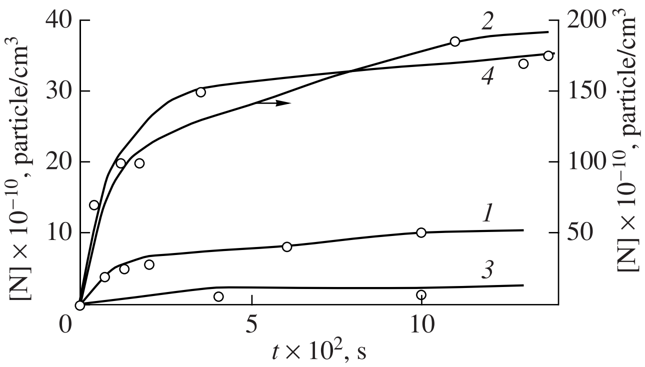

Fig. 2. Complex concentration on the target as a function of the contact time: (*1*, *3*) no irradiation and (*2*, *4*) UV irradiation for 7 h. The ZnO compaction pressure is (*1*, *2*) 400 and (*3*, *4*) 1500 kgf/cm^2.

complex concentration is also dependent on the ZnO tablet compaction pressure. As is shown in Fig. 3, $\ln\frac{[N]_0}{[N]_0 - [N]}$ in any run is a linear function of t (target temperature 373 K) and is thus in agreement with Eq. (3).

From the slopes of the straight lines plotted in Fig. 3, we determined the average rate constant of complex decomposition on the ZnO target for each run.

The UV preirradiation of the target increases the decomposition rate constant k_{het} by a factor of ~2 (Table 1). Raising the compaction pressure from 400 to 1500 kgf/cm^2 decreases k_{het} by a factor of ~5, irrespective of whether UV radiation is used.

Effect of UV Irradiation on the Concentration of the Zn-Containing Complex

The concentration of the Zn-containing complex in the gas phase increases in proportion to the UV irradiation time t_{irr} (Table 2).

Our experimental data led us to the following inferences:

(1) It is likely that the UV irradiation of the target surface excites local F^+ centers [5–8], which serve as efficient H_2O_2 adsorption sites.

Table 1. Rate constant of the decomposition of the complex for the UV-preirradiated and unirradiated targets as a function of the target compaction pressure (P, kgf/cm^2)

P, kgf/cm^2	k_{het}, s^{-1}	
	no irradiation	UV irradiation (t_{irr} = 7 h)
400	113.5	248.4
1500	23.0	48.8

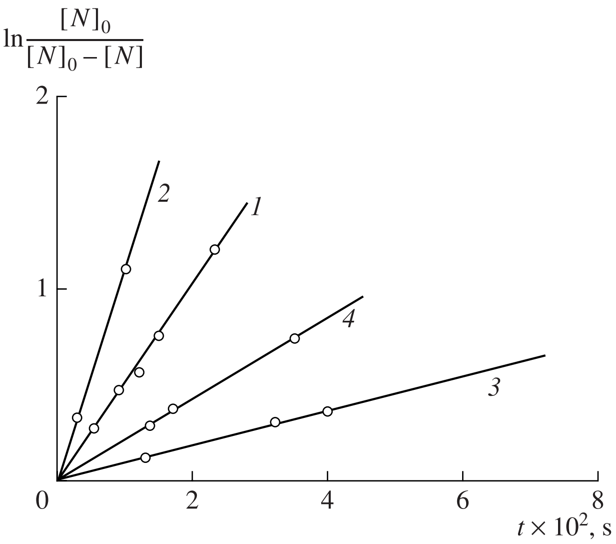

Fig. 3. $\ln\frac{[N]_0}{[N]_0 - [N]}$ as a function of t at a target temperature of 373 K: (*1*, *3*) no irradiation and (*2*, *4*) UV irradiation for 7 h. The ZnO compaction pressure is (*1*, *2*) 400 and (*3*, *4*) 1500 kgf/cm^2.

(2) The activation of the surface centers enhances both the decomposition of H_2O_2 and the Zn-containing complex and the emission of heavy particles (atoms, ions, and clusters) from the surface [10].

Decomposition of the Zn-Containing Complex on the Quartz Substrate

In all runs at 360–423 K, ln[N] is a linear function of t (Fig. 4) and is thus in good agreement with Eq. (4).

It follows from the linearity of ln[N] versus t that the decomposition of the complex obeys a first-order rate law. From the slopes of the straight lines plotted in Fig. 4, we derived k_n for each temperature examined. The data thus obtained are listed in Table 3.

Experimental data indicate that more than 98% of the complex decomposes on the substrate at $T \geq 423$ K. The temperature dependence of the decomposition rate constant obeys the Arrhenius law, which governs the activated processes:

$$k = k_0 e^{\frac{E_a}{RT}}.$$

The logarithm of the decomposition rate complex is a linear function of $1/T$: $\log k = \log k_0 - \frac{E_a}{RT}$. From this equation, we derived the activation energy E_a and the preexponential factor k_0. The basic equation of activate

Table 2. Amount of ZnO deposited on a Si(111) substrate (a) as a function of the UV irradiation time ($P = 400$ kgf/cm^2)

t_{irr}, h	a, µg	$[N] \times 10^{-11}$, particle/cm^3
0	111.7	1.05
2	538.6	5.19
4	912.0	9.95
7	1602.3	18.60

Table 3. Rate constant of the decomposition of the complex (k_n) on the quartz substrate and the lifetime of the complex (τ) as a function of temperature (T)

T, K	k_n, s^{-1}	k_{irr}, s^{-1}	E_a, kJ/mol	τ, s
360	19.2	–	–	0.0521
373	38.6	–	–	0.0259
393	133.1	0.4×10^{12}	64.33	0.0075
406	278.8	–	–	0.0036
423	444.4	–	–	0.0022

complex theory for a monomolecular reaction can be written as

$$k = \chi\frac{k_B T}{h}\left(1 - e^{\frac{h\nu}{kT}}\right)e^{-\frac{E_a}{RT}}\ [11],$$

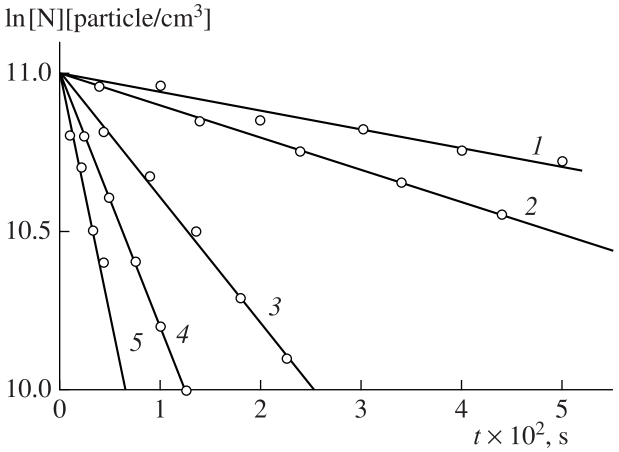

Fig. 4. ln[N] as a function of t for the decomposition of the complex on the quartz substrate at (*1*) 360, (*2*) 373, (*3*) 393, (*4*) 406, and (*5*) 423 K.

where χ is the transmission coefficient, k_B is the Boltzmann constant, h is Planck's constant, T is absolute temperature, ν is the vibration frequency, E_a is the activation energy, and R is the universal gas constant.

The preexponential factor $\left(k_0 = \chi\frac{\kappa T}{h}\left(1 - e^{\frac{h\nu}{kT}}\right)\right)$ was calculated to be 10^{12}–10^{13} s^{-1}. The experimental k_0 value for the decomposition of the Zn-containing complex is 0.4×10^{12} s^{-1}, which is in agreement with the value following from activated complex theory [11]. This is further evidence that the decomposition of the Zn-containing complex is a first-order reaction.

The fact that the activation energy of the decomposition of the Zn-containing complex (64.3 kJ/mol) is similar to that of hydrogen peroxide decomposition (79 kJ/mol) suggests that the complex has a peroxide-like structure [12].

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