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Investigation of Sintering Kinetics of ZnO by Observing Reduction of the Specific Surface Area

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Abstract:

Reduction of the specific surface area of porous ZnO during the sintering process was studied. ZnO powder was sintered at temperatures from 673 K to 1173 K. The decrease in the specific surface area was observed as a function of temperature and sintering time. Two different models were involved in order to define the appropriate parameters. The Arrhenius equation was used to give information on the activation energy of sintering. The LSE method was applied for determining optimum parameter values.

Keywords: Sintering, Kinetics, Specific surface area, ZnO

Introduction

ZnO is a stable compound with a wurzite-type hexagonal structure. It is piezoelectric and piezoelectric. For certain preparation conditions it has characteristics of a dielectric, i.e. a n-type semiconductor [1]. ZnO shows a pressure-induced phase transition from wurzite (P6₃mc) to the rocksalt (Fm3m) phase in the 10 GPa ranges [2]. Zinc oxide is a multifunctional material with a wide range of applications such as varistors (because of its exceptional nonlinear ohmic characteristics [3]), gas sensors, piezoelectrics, and electrodes for solar cells and optoelectronic devices [4]. It is also used for transparent conducting films, and efficient sun block coatings for human skin protection [2].

During disperse mixture heating, a complex process of sintering takes place. During the sintering process, it is possible to obtain a more or less porous materials, although a highly porous or more dense structure can be obtained using special heat treatment [5]. Most commonly, the sintering process can be defined as a process, which causes growth of material particles, during heating to a temperature, which is lower than the melting temperature. Sintering causes both the specific surface area and porosity to decrease and the density to increase. Sintering occurs in three stages; in the initial stage, areas of contact between adjacent particles form and grow. In the intermediate stage, growing necks merge and the large number of small particles is replaced by a smaller number of large particles. In the final stage of sintering, the pore spaces become broken up with isolated closed pores remaining, which shrink in size as densification proceeds [6].

German and Munir [7] proposed a model of interparticle neck shape during sintering. Through this model, various geometric parameters were interrelated precisely. An important result of this approach is that the kinetic dependence for the rate of surface area reduction on

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the sintering mechanism has been established. Thus, the mass transport process can be identified via the kinetics of the specific surface area reduction.

Compared to neck size and shrinkage measurements, surface area offers several advantages as a sintering-process monitor, because surface area reduction accompanies all sintering mechanisms, and it is an easily measurable quantity. Surface area as a sintering parameter is most appropriate for disperse particles, a size region where it is difficult to measure the neck diameter.

The basis for using surface area monitoring in the intermediate stage is the statistical sintering model of Kuczynski [8]. In this model pore-elimination and grain growth processes are coupled to explain the intermediate and final stages of sintering.

This problem was dealt with by D. Nicholson [6], Hartman et al. [9] and other authors.

In this paper we analyzed the sintering kinetics of ZnO by observing reduction of the specific surface area. The proposed models enabled us to correlate relations between characteristic parameters for this material such as the specific surface area and the sintering time and temperature.

Experimental procedure

Commercially available ZnO powder (99%, p. a. Merck) was used. The powder was compacted using a uniaxial double action pressing process in a 6 mm diameter tool (Hydraulic press RING, P-14, VEB THURINGER). The compaction pressure was 0.5t/cm².

Compacts were placed in an alumina boat and heated in a tube furnace (Lenton Thermal Design Typ 1600). Compacts were sintered isothermally for 5, 15, 30, 60 and 120 minutes in the temperature range from 673 K to 1173 K.

Specific surface area was measured using the BET method.

Results and discussion

The average initial value of the specific surface area of green samples was $S_0=3.95 \text{ m}^2\text{g}^{-1}$. The measured values of the specific surface area of sintered samples are given in Tab. I.

Tab. I Values of specific surface area (m^2g^{-1}) of sintered ZnO samples

T(K)/t(min)	5	15	30	60	90	120
673	3.81	3.69	3.65	3.62	3.60	3.59
773	3.78	3.60	3.41	3.26	3.20	3.19
873	3.52	3.06	2.75	2.54	2.39	2.34
973	3.30	2.71	2.31	1.65	1.40	1.43
1073	2.68	1.83	1.40	0.92	0.62	0.39
1173	2.01	1.22	0.67	0.39	0.30	0.29

During analyses of experimentally gathered results, we used two models to describe changes of specific surface area with sintering time. According to D. Nicholson's model [6]:

$$\frac{\Delta S}{S_0} = \left(\frac{\Delta S}{S_0} \right)_{\max} \cdot (1 - e^{-kt}) \quad , \text{where} \quad \left(\frac{\Delta S}{S_0} \right)_{\max} = \frac{S_0 - S_e}{S_0} \quad (1)$$

where: S - the specific surface area of sintered specimens, S_0 - the starting specific surface area, $\left(\frac{\Delta S}{S_0}\right)_{\max}$ - the maximum relative change of specific surface area, S_e - equilibrium value of specific surface area, k - the sintering rate constant, t - the sintering time.

Using equation (1), D. Nicholson connected the specific surface area, time and sintering temperature and verified his model with data on sintering of magnesium oxide and iron oxide [6]. Both the sintering rate constant and equilibrium surface area are functions of temperature and must be determined experimentally.

The second model which we used in our research was the equation proposed by Hartman et al. [9]:

$$\frac{\Delta S}{S_0} = \left(\frac{\Delta S}{S_0}\right)_{\max} \cdot [1 - (1 - k \cdot t)^a] \quad (2)$$

where: S - the specific surface area of sintered specimens, S_0 - the starting specific surface area, $\left(\frac{\Delta S}{S_0}\right)_{\max}$ - the maximum relative change of specific surface area, S_e - the equilibrium value of specific surface area, k - the sintering rate constant, t - the sintering time, a - a parameter which depends on temperature and is defined as $a = \frac{1}{1-n}$, where n is the reaction order, i.e. mechanism - characteristic exponent which is dependent on the mass transport process.

Fig. 1. represents the results of sintering analyses of ZnO according to eq. (1).

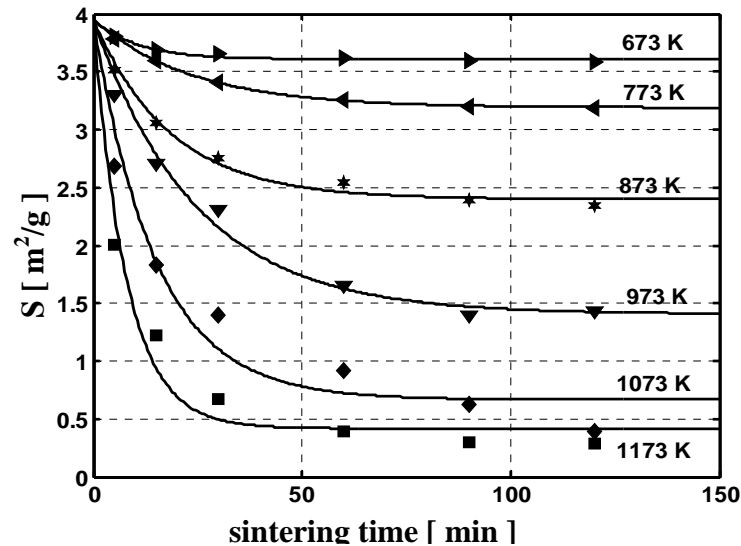


Fig.1 Reduction of specific surface area of ZnO according to eq. (1)

Tab. II shows the calculated values of corresponding parameters using eq. (1).

Tab. II Values of parameters k , S_e and L_{\min} using eq. (1)

par/T(K)	673	773	873	973	1073	1173
k	0.0942	0.0420	0.0542	0.0441	0.0673	0.1273
S_e	3.6000	3.1900	2.4000	1.4060	0.6673	0.4184
L_{\min}	0.0013	0.0009	0.0174	0.0682	0.3179	0.2160

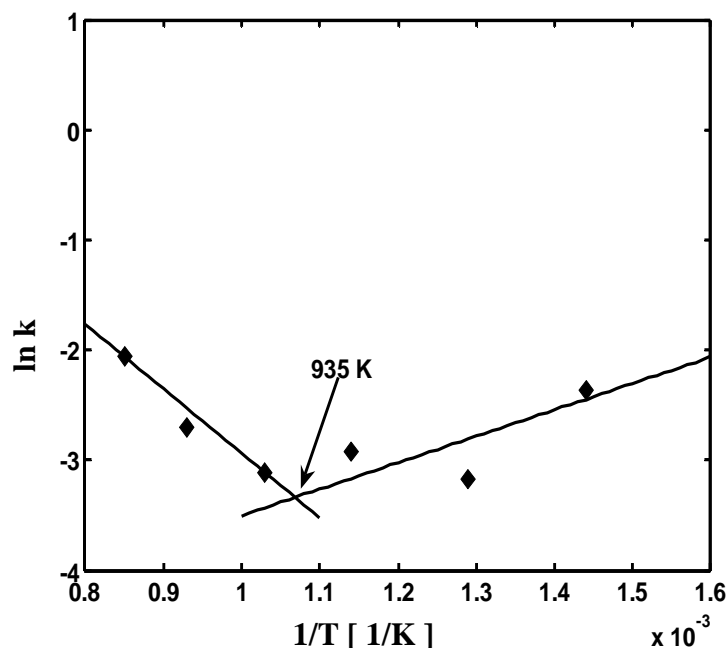
**Fig. 2** Diagram of $\ln k$ as a function of $1/T$

Fig. 2. shows the $\ln k$ dependency on $1/T$. The function minimum at ~ 930 K implies a possible change of the sintering mechanism at that temperature. At lower temperatures, the constant rate is higher due to a higher specific surface area, so there is a greater possibility of atomic movement on the surface. This implies that at lower temperatures the surface diffusion sintering mechanism is taking place, and that, starting from ~ 930 K, volume diffusion has the major role during the sintering process.

The activation energy of sintering was calculated assuming the two mechanisms described above, using the Arrhenius equation [6]:

$$k = k_0 \cdot e^{-\frac{E_a}{R \cdot T}} \quad (3)$$

where: k – the rate constant, k_0 – the preexponential constant, E_a – the activation energy, R – the gas constant (8.314 J/Kmol) and T – the sintering temperature. The values obtained using eq. (3) are, $E_a \sim 20$ kJ/mol for surface diffusion, and $E_a \sim 49$ kJ/mol for volume diffusion.

These values confirm the assumption that on lower temperature surface diffusion is the dominant mechanism during the sintering process, and on higher temperatures volume diffusion mechanism is the dominant mechanism, which demands higher energy consumption. As we mentioned before, a greater possibility of atomic movement is on the grain surface rather than within atoms that are placed inside the grain. Therefore, lower energy is required for atomic movement on the surface than within the grains.

Fig. 3. shows results of sintering analyses of ZnO according to eq. (2).

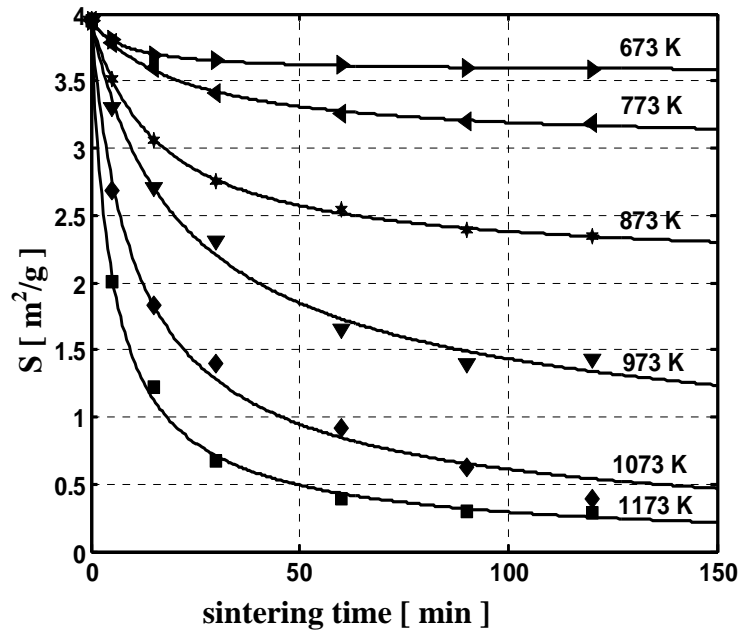


Fig. 3. Reduction of the specific surface area of ZnO according to eq. (2)

Tab. III Calculated values of corresponding parameters according to eq. (3)

par/T(K)	673	773	873	973	1073	1173
S_e	3.5700	3.0200	2.1100	0.4000	0	0
k	0.1290	0.0450	0.0670	0.0740	0.1340	0.2590
a	-0.9900	-0.9900	-0.9400	-0.5800	-0.7000	-0.7900
n	2.0101	2.0101	2.0638	2.7241	2.4285	2.2658
L_{\min}	0.0002	0.0013	0.0011	0.0374	0.0510	0.0147

Fig. 4. (a) shows $\ln k$ as a function of $1/T$. We can notice similar behavior as in the case of Nicholson's equation, and a minimum at ~ 900 K. Calculated activation energies for these two mechanisms of sintering are: $E_a \sim 20$ kJ/mol for surface diffusion, and $E_a \sim 57$ kJ/mol for volume diffusion.

Values of activation energies for mentioned sintering mechanisms do not differ significantly from those calculated from the first model, which also confirms conclusions stated for the previous one.

Changes of parameter n with the sintering temperature are shown on Fig. 4. (b). We can notice that this parameter has change in slope at ~ 920 K, which indicates that a change in the sintering mechanism happens approximately on this temperature.

L_{\min} is a sum of deviation squares of measured data and the assumed theoretical curve. Comparing values for L_{\min} for these models, which are given in Tab. IV, we can notice a lower deviation for the second model, which has three parameters, and because of that better fits experimental data, i.e. better describes the selected processes.

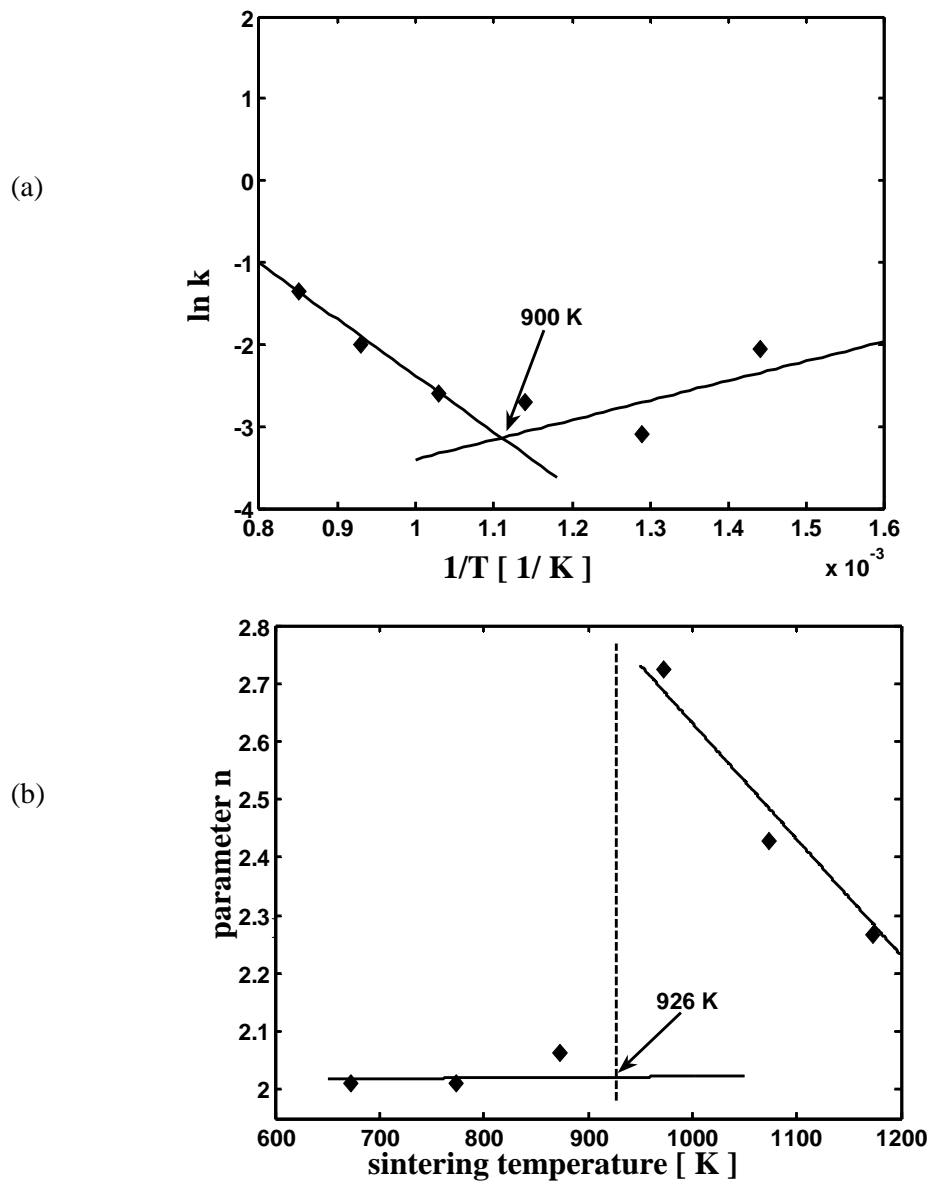


Fig. 4 Diagrams (a) $\ln k$ and (b) n as functions of $1/T$

Tab. IV Values of L_{\min} for observed two models in function of sintering temperature

Model/T(K)	673	773	873	973	1073	1173
D. Nicholson	0.0013	0.0009	0.0174	0.0682	0.3179	0.2160
M. Hartman	0.0002	0.0013	0.0011	0.0374	0.0510	0.0147

Conclusion

In this paper a possible use of phenomenological equations in analyses of sintering kinetics of porous ZnO was analyzed by observing reduction of the specific surface area according to models of Nicholson and Hartman et al. We concluded that the second model

slightly better fits experimental data obtained by measuring the specific surface area. A change of sintering mechanisms from surface diffusion to volume diffusion was noted in temperature interval 900 – 950 K, which has been confirmed with the results obtained based on these two equations. Activation energies calculated using both equations are similar. Unfortunately, we found no literature data on application of these equations on sintering kinetics of ZnO so we couldn't compare our results with literature data. According to our analyses, we suggest usage of these two equations in order to determine the sintering kinetics and sintering mechanisms of some other systems as well.

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Садржај: У овом раду проучавано је смањење специфичне површине цинк-оксида током процеса синтеровања. Прах ZnO је синтерован у температурном интервалу од 673 до 1173 K. Смањење специфичне површине је посматрано у функцији од температуре и времена синтеровања. Примењена су два модела приликом одређивања одговарајућих параметара. За израчунавање енергије активације синтеровања коришћена је Аренијусова једначина. LSE метод је примењен за одређивање оптималних параметара карактеристичних за процес синтеровања.

Кључне речи: Синтеровање, Кинетика, Специфична површина, ZnO.
