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Thermodynamic Properties of Ar Film on ZnO Metal Oxide Powders Measured by Adsorption Isotherms

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Abstract. Adsorption and thermodynamic properties of Ar on ZnO powder were studied using a newly built gas adsorption isotherm apparatus, which has good temperature stability within 0.01 K in a wide rage (20–300 K) and good pressure accuracy with a resolution better than 10^{-5} in 100 torr. Two distinct Ar atomic layers were measured. A specific surface area of the ZnO particle was also obtained from calculations of a molecular area of Ar on the surface of the adsorbents, and found to be approximately 100 m^2/g. The thermodynamic results including the 2-dimensional compressibility indicate the surface melting occurs near 77 K.

Keywords: adsorption, ZnO, Ar

1. Introduction

Adsorption studies of noble gases on metal oxide surfaces are interesting because the interaction of simple molecules with the surface provides fundamental knowledge to understand the structural development from the two dimensional film to the three-dimensional lattice. The aim of the study becomes more interesting if the surface interacts with simple/toxic gases due to the fact that the results from this study enhance our understanding of the gas-surface interactions that can subsequently be applied to the study of catalytic reactions aimed at reducing atmospheric pollutants. Furthermore, the study of the interaction of small molecules with metal oxide surfaces has implications in a wide range of technologically important areas, such as catalysis and lubrication (Henry et al., 1994).

ZnO is a new candidate material for its potential application on semiconductors and pollutant scrubbers. The potential area of its technical application becomes even larger if it is doped on pure metal oxides. There are several adsorption studies of various gases on a ZnO surface (Becker et al., 2000; Guo et al., 1997; Anderson and Nichols, 1986; Konenkamp et al., 2000; Jun et al., 1992; Na et al., 1992). Many authors (Shozo et al., 1978; Yasunori et al., 1995; Kolodney et al., 1988; Yasunori et al., 1999; Xin et al., 1999; Christiana et al., 2002) have made investigations into the molecular configurations of Ar on metal oxides including MgO etc. However, to the best of our knowledge, no direct study on the physical/chemical interaction of noble gases on ZnO has been reported. Thus, in this article we focus on the interaction of Ar adsorbed on ZnO with the purpose of characterizing the thermodynamic properties. Adsorption isotherm studies have been used to investigate the wetting and layering properties of atomic and molecular films on ZnO. These thermodynamic measurements enable us to characterize the interplay between adsorbate-adsorbate and adsorbate-substrate interactions. A longer-term goal of this work is to obtain an understanding of the surface mediated physical reactions of Ar with pure and doped nano or meso sized ZnO particles.

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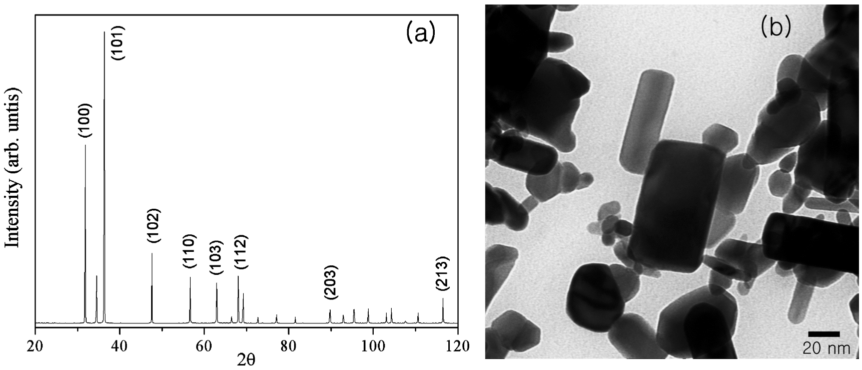

Figure 1. (a) A plot of synchrotron based X-ray diffraction pattern taken from the ZnO powder. All peaks are corresponding to ZnO phase, while only representative peaks are indexed. (b) A typical morphology picture of grains taken by TEM.

2. Experimental Details

2.1. Sample Preparation

ZnO powder, which was obtained from a commercial source (Sigma-Aldrich, 99.999%), has an hcp structure (a = 3.25 Å, c = 5.21 Å) with a narrow size distribution around a few hundreds nano meters. The X-ray diffraction pattern and typical morphology of the powder is shown in Fig. 1. X-ray diffraction data were taken in the transmission mode ($\lambda = 1.542$ Å) using a multi channel analyzer detector at the High Resolution Powder Diffraction (HRPD) beamline of the Pohang Light Source (PAL). The morphology picture of the sample taken by TEM reveals that the typical size of the powder is between 20–100 nm which matches with the estimations measured by a full width at half maximum (FWHM) of the main peaks at XRD patterns (Warren, 1941).

Prior to adsorption, all ZnO powders were baked below 400°C for 6 hours under vacuum ($<10^{-7}$ torr) to eliminate impurities that evolve from the surface (e.g. physisobed CO, and H_2O). The quality and specific surface area of the powders were then determined by using nitrogen adsorption isotherms. Our experience with certain adsorbates, methane on MgO for example (Larese, 1998), has shown that the quality of the powder is related to the number of uniform steps measured from the adsorption isotherms.

2.2. Isotherm Measurements

All adsorption isotherm data were collected using a newly built gas-handling apparatus. The equilibrium pressure was obtained by waiting 10 minutes after delivering the desired small amount of gas (≈4 cc) to the sample cell made of copper. During an isotherm the temperature of the sample cell was controlled and monitored by using a temperature controller (LakeShore 340) with better than 5 mK stability. The pressures were measured by two different (100 and 1000 torr) capacitance manometers (MKS Baraton). The volume of the dead space of the cell (a few cm^3) was determined by using successive helium gas expansions from the calibrated dosing volume (37.43 cm^3).

To calculate the 2-dimensional compressibility (K_{2D}) and the isosteric heat of adsorption (Q_{st}), measured isotherm data were calibrated by a fitting procedure. The reason is that the total surface area of the individual samples varied somewhat depending on the amount of powder. The data were fit to a smooth curve using a commercial interpolation package (Kaleidagraph®). The calculation of Q_{st}, which by definition is at constant coverage, is difficult because the points in isotherms measured at different temperatures are not at exactly the same coverage. This fitting procedure is therefore necessary because it allows the comparison at a nominally constant coverage, without large errors, so long as the gaps between points in an isotherm are not too large. Further, at the first vertical rise, the vapor pressure of Ar is quite low, i.e. it approaches the resolution of the capacitance gauges and temperature stability of the system, so the interpolation gives a more accurate measurement over this region of an isotherm.

3. Results and Discussions

Ar isotherms were measured over the temperature range from 57 K to below the triple point (83.78 K), and

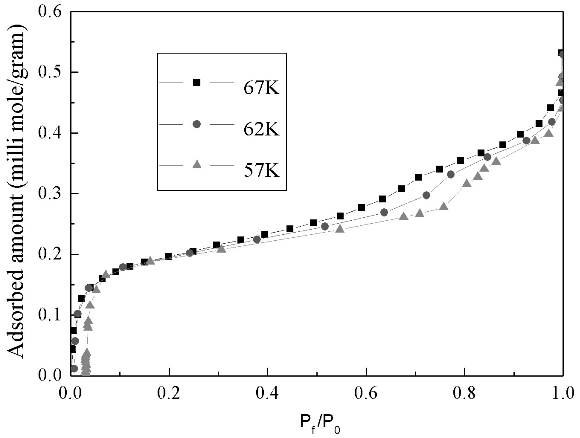

Figure 2. Isotherm measurements of Ar on ZnO powder surface at different temperatures.

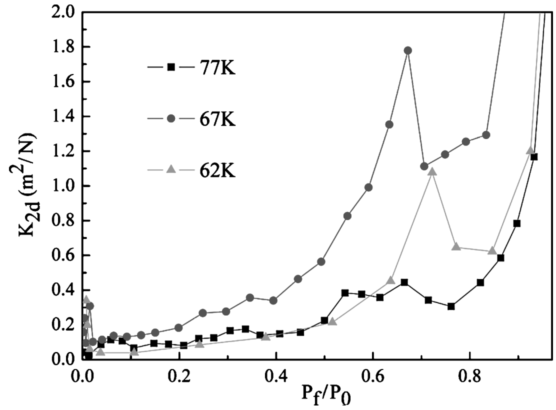

Figure 3. A plot for 2-dimensional compressibility peaks of Ar film on ZnO surface. The formation of the second layer is clearly seen near $P_f/P_0 \approx 0.72$.

the results are shown in Fig. 2 as a function of pressure normalized by its saturation vapor pressure (P_f/P_0). Two distinct Ar layers are clearly visible, and the existence of the second layer is more evident as the temperature is lowered. Only by the isotherms, however, it is difficult to demonstrate the existence of reentrant first-order layering transition phenomena, which was reported by Youn et al., on graphite (Youn and Hess, 1990). This may be due to either an intrinsic adsorption property of Ar on ZnO or a poor quality of the powder which contains round edges of the particles. It is known that the sharpness and number of steps are reduced if the powder has a wide range of particle sizes or the shape of the particle is not uniform.

It is possible to estimate the molecular cross section (or area per molecule) by measuring an exact monolayer step height in isotherms. The molecular cross section of Ar on the ZnO surface is about 3.5 Å^2. Two important thermodynamic properties, the 2-D compressibility (K_{2D}) and the isosteric heat of adsorption, (Q_{st}), are obtained from the measured isotherms. The calculation of K_{2D} is important because it shows the response of the Ar film to a change in spreading pressure. It is defined as;

$$K_{2D} = \frac{AP}{RTN}\frac{dN}{dP} \tag{1}$$

where A, P, R, T, N, are the surface area of the substrate, measured pressure, gas constant, temperature, and the number of adsorbed molecules, respectively. This quantity can be used to investigate where phase transitions (such as melting and layering) take place in the film since the derivative in Eq. (1) becomes large at isotherm steps. In general, broad, weak peaks in the compressibility (plotted as a function of equilibrium vapor pressure or chemical potential) are associated with liquid layers whereas solid layers show sharp intense peaks. Thus, monitoring the height and the full width at half maximum (FWHW) of K_{2D} as a function of temperature can be an indication of the location of melting transitions within the adsorbed layers. Figure 3 shows the K_{2D} as a function of normalized equilibrium vapor pressure for the first and second adsorption steps. All of the isotherms exhibit compressibility peaks in these regions although the peaks include noise coming from the difficulty of measuring low vapor pressures. It is notable that the peaks near the second layer completion ($P_f/P_0 = 0.72$) are more evident than the ones in the isotherm measurements. Interestingly, the second layer formation becomes less significant at 77 K, which strongly suggests surface melting.

Another important thermodynamic quantity related to a layer growth is the *isosteric* (constant coverage) heat of adsorption, Q_{st}. This quantity represents the work required to bring a molecule from infinity (or equivalently the three-dimensional vapor) onto the adsorbing surface. It is defined by

$$Q_{st} = RT^2 \left.\frac{\partial \ln p}{\partial T}\right|_x \tag{2}$$

This relation can be derived from the thermodynamics of adsorbate on substrate using the method

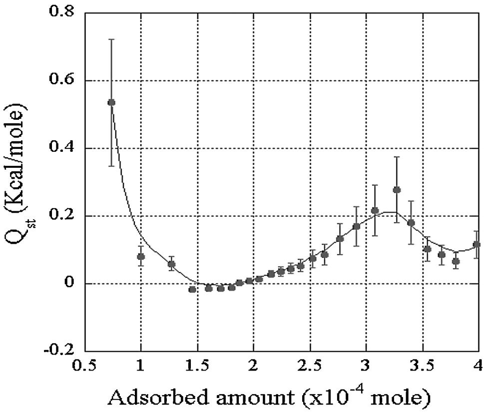

Figure 4. The calculation result of Q_{st} values of Ar on ZnO powder at 67 K.

presented by Hill (1949). Note that the derivative is taken at constant coverage χ. The calculation of Q_{st} requires the fitting of the isotherms to a polynomial as described elsewhere (Freitag et al., 2000), so that they may be compared at constant coverage. Figure 4 shows the variation of Q_{st} at 67 K as a function of the amount of Ar adsorbed on the ZnO surface.

The peak corresponding to the first layer condensation is readily observed, while a smaller peak is also observed near the second layer completion. It is worthwhile to note that the height of the peaks decreases while increasing the temperature, suggesting stronger adhesion between Ar and the surface at a lower temperature: it requires less energy to bring Ar from infinite distance to the ZnO surface.

Again, it must be noted that obtaining an accurate Q_{st} value by the adsorption experiment is difficult due to the fact that, by definition, Q_{st} is strongly affected by the differences between isotherms measured at different temperatures. Furthermore, keeping the sample at exactly the same temperature throughout the isotherm period is technically difficult. The difficulties were enhanced for higher temperature ones that requires longer isotherm data collection periods and do not show clear saturation vapor pressure.

4. Conclusion

For the first time, adsorption and thermodynamic properties of Ar on ZnO powder were studied. Two distinct Ar atomic layers were measured. The existence of the second layer was clearly demonstrated by a calculation of 2-dimensional compressibility peaks. Surface melting was observed near 77 K. A specific surface area of the ZnO particle was also measured and shown to be approximately 100 m^2/g.

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