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In situ x-ray diffraction study of the thermal expansion of silver nanoparticles in ambient air and vacuum

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The thermal expansion behavior of silver nanoparticles in ambient air and vacuum was studied by *in situ* x-ray diffraction (XRD) measurement of the particles dispersed within mesoporous silica in the temperature range of 25–700 °C. It has been shown that thermal expansion coefficient of Ag nanoparticles in vacuum is about $0.6\times10^{-5}/°C$, only near one fourth that of bulk silver ($2.2\times10^{-5}/°C$). However, the coefficient in air is about $1.7\times10^{-5}/°C$, about 3 times as high as that in vacuum and close to the value of bulk Ag. These were explained in terms of Ag particles' surface energy, oxygen surface adsorption, and dissolution into lattice. This study is of importance in architectonics of future nanodevices. © *2005 American Institute of Physics*.

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Ag nanoparticles exhibit many unique chemical and physical properties, and have applications in many fields, such as, optical devices,[1,2] gas sensors,[3,4] catalysis,[5,6] and surface-enhanced Raman substrate.[7,8] Extensive study has been done in optical properties, catalysis, and environmental sensitivity. The lattice constant of Ag nanoparticles and its size dependence have also been studied, such as, by extended x-ray-absorption fine structure (EXAFS) technology when the particles are in solid argon,[9] by high resolution transmission electron microscope (TEM) when the particles are embedded in glass,[10] and by electron diffraction when the particles on carbon substrate.[11] It has been revealed that variation of lattice parameters are of importance in the size evolution of the surface plasmon resonance of Ag nanoparticles.[12]

As we know, nanoparticles could be used for the building blocks of various future nanodevices. Obviously, the corresponding thermal expansion behavior would be very important for the structural design, thermal stability, and reliability of such devices. However, the lattice thermal expansion of silver nanoparticles in different environments has not been reported so far. Recently, putting Ag nanoparticles into the pores of silica mesoporous solid, which is a weak interacting medium to Ag,[1] and whose pores are interconnected and open to ambient air, we have investigated the lattice thermal expansion of the quasi-free silver nanoparticles in air and vacuum by *in situ* x-ray diffraction (XRD) measurement, and found that the thermal expansion for the quasi-free silver nanoparticles is much smaller in vacuum than that in air, and both cases are smaller than that of bulk Ag. This study is of importance not only in fundamental academic interest, but also in architectonics of future nanodevices since the nanoparticles could be used as building blocks. The details are reported in this letter.

The monolithic mesoporous silica host (planar-like, about 1.5 mm in thickness) was first prepared by a sol–gel technique with precursors: tetraethylorthosilicate, water, alcohol (catalyzed by HNO_3), followed by drying, and finally annealing at 700 °C for 1 h, as previously described.[13,14] The mesoporous silica prepared in this way, whose pores are interconnected and open to ambient air, had the porosity of about 50%, a specific surface area of 560 $m^2\,g^{-1}$, and pore diameters mainly distributed in the range below 20 nm, determined by isothermal N_2 adsorption measurement, as previously described.[15] The host was then soaked into silver nitrate ($AgNO_3$) aqueous solution with 0.5M for 5 days, and taken out for heat treatment in H_2 at 600 °C for 1 h in a quartz tube oven. The Ag nanoparticles are thus *in situ* formed within pores of silica mesoporous solid. The loading amount of Ag in the host was estimated to be 2.4% in weight from the host porosity and concentration of the soaking solution, without considering the loss of Ag during its preparation.[14]

In situ XRD measurements for the treated samples were performed at different temperatures in ambient air or vacuum condition on X'Pert Pro MPD diffractometer with a sample holder, which can be heated and evacuated (10^{-5}–10^{-4} mbar). CuK_α radiation was used, and Si(220) diffraction line was chosen as a reference line for the calibration of the diffraction position. Samples were ground into powders, mixed with a small amount of pure Si powders for calibration, before XRD measurement. The measurement temperature range in this study is 25–700 °C. The temperature control is within ±1 °C. Temperatures were kept constant for 30 min before each measurement.

The existence of loaded silver particles inside pores of silica has been confirmed by the fact that the isothermal nitrogen sorption for H_2 heat-treated soaked sample is lower than that for SiO_2 host, as previously illustrated.[15] Ag particles dispersed in silica are approximately spherical in shape, and of about 5 nm in mean size observed by TEM.

Figure 1 shows the *in situ* measured XRD spectra of the Ag-loaded sample at different temperatures in ambient air and vacuum conditions, respectively. It can be seen that the diffraction peak of the Ag(111) for both cases shifts to smaller angle with increase of temperature, indicating the lattice thermal expansion. The lattice parameter of Ag nanoparticles as a function of temperature for both cases is shown in Fig. 2, in which the corresponding data of bulk Ag is also

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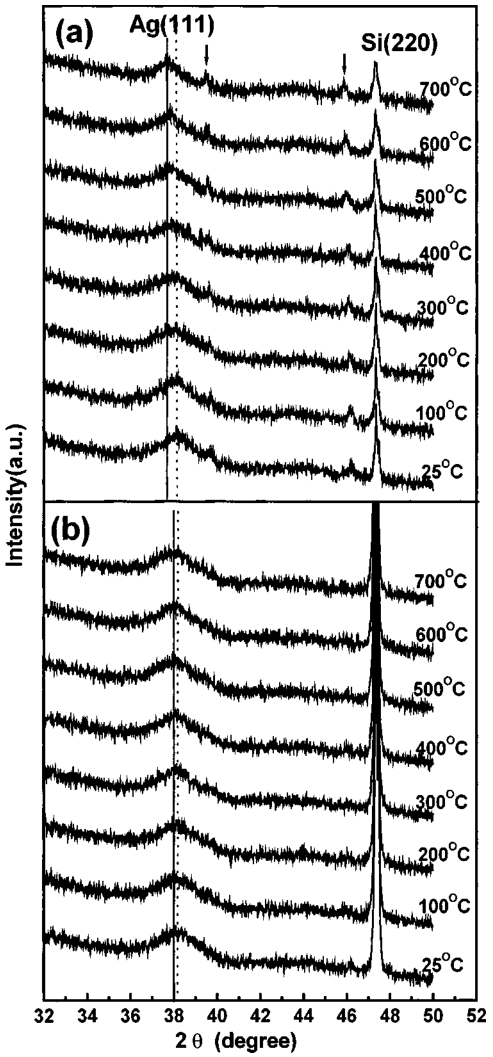

FIG. 1. The XRD patterns of silver nanoparticles in (a) ambient air (arrows: denotes the diffraction peaks from sample holder) and (b) in vacuum.

included. In the studied temperature range, the lattice constant of Ag nanoparticles in air is larger than that in vacuum but smaller than that of bulk at the same temperature, and the differences between them increase with rising temperature. It can be seen from Fig. 2 that the evolution of lattice constant shows roughly linear relation with increasing temperature. We can thus obtain the lattice thermal expansion coefficients, which are 1.7×10^{-5} and $0.6 \times 10^{-5}/°\mathrm{C}$ for Ag nanoparticles in ambient air and vacuum, respectively, in the temperature range of 25–700 °C. The value in ambient air is 3 times as high as that in vacuum case. Both cases are lower than that of bulk Ag which is about $2.2 \times 10^{-5}/°\mathrm{C}$ in the same temperature range.[16]

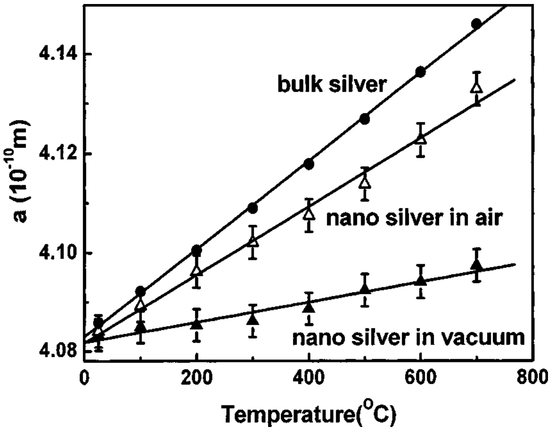

FIG. 2. The plots of silver lattice parameter, calculated from Ag (111) diffraction in Fig. 2, vs temperature. Solid line: linear regression.

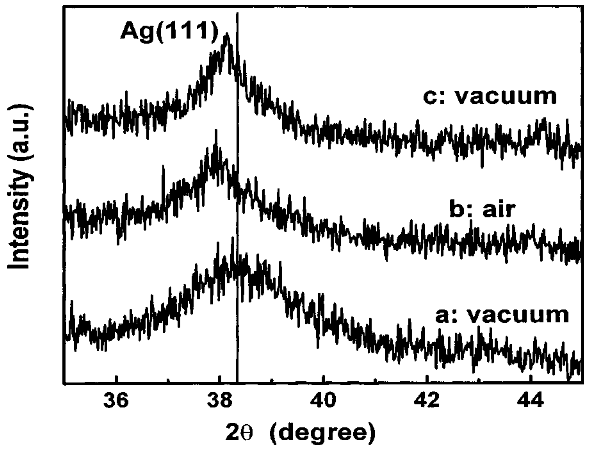

FIG. 3. XRD patterns of silver nanoparticles (a) before and (b) after exposure to ambient air for 50 min at 700 °C. Curve (c): the result after evacuation for 50 min at 700 °C for sample (b).

In addition, if the environment of sample changes from vacuum to ambient air at the same temperature, the diffraction peak position will shift significantly, especially at high temperature. Figure 3 illustrates the results measured before and after exposure to ambient air for 50 min at 700 °C. We can see that the diffraction peak of the Ag(111) obviously shifts to a smaller angle when the environment of sample changed from vacuum to ambient air. If subsequently observed under vacuum again (20 min or longer after evacuation), the peak moves back to a larger angle but cannot reach its original position, as shown in curve (c) of Fig. 3.

Now let us make a brief discussion. As we know, with decrease of particle size, the surface effect will get more and more significant. Obviously, the surface tension of a particle will induce variation of lattice constants and thermal expansion coefficient. Furthermore, any factor, leading to change of the surface energy of particles, should induce variation of lattice constants and thermal expansion coefficient, such as, adsorption of molecules on the particles during environmental exposure.

As mentioned above, the lattice constant and lattice thermal expansion coefficient of silver nanoparticles in vacuum are less than those of bulk silver. This could be attributed to the surface tension of Ag particles. It is well known that the hydrostatic pressure P within a spherical particle, induced by the surface tension, can be expressed as[17] $P = 2\gamma/R$, where γ and R are the surface tension and radius of the particle, respectively. Because the compressibility of solid is defined by $\kappa = -\Delta V/PV$, for a spherical particle with cubic crystal structure, we have the relation[18]

$$\frac{\Delta a}{a} = -\frac{1}{3}\kappa P = -\frac{2\kappa\gamma}{3R}, \tag{1}$$

where V is the volume and Δa is the change in lattice constant a due to the surface tension. So the surface tension will induce lattice contraction. Obviously, when R is small enough, P value will be large sufficient to induce detectable lattice contraction. Furthermore, the pressure dependence of thermal expansion coefficient can be described by Anderson relation[19–21]

$$\frac{\beta(T,P)}{\beta(T,0)} = \left[\frac{V(T,P)}{V_0(T,0)}\right]^{\delta_T(T,P)}, \qquad (2)$$

where $\beta(T,P)=(1/V)(\partial V/\partial T)_P$ is the volume thermal expansion coefficient, $\delta_T(T,P)=-(1/\beta B_T)(\partial B_T/\partial T)_P$ is the so-called Anderson–Gruneisen parameter and >0, B_T is isothermal bulk modulus, T is the absolute temperature, and $V(T,P)=V_0(T,0)+\Delta V$. Combining Eq. (1), we can rewrite Eq. (2) as

$$\beta(T,P) = \beta(T,0)[1-\kappa P]^{\delta_T(T)} = \beta(T,0)\left[1-\frac{2\gamma\kappa}{R}\right]^{\delta_T(T,P)}. \qquad (3)$$

Here, $\beta(T,0)$ corresponds to the value of bulk silver, while $\beta(T,P)$ to that of silver nanoparticles with surface effect in vacuum. Since the data of the parameters γ, κ, and δ for Ag nanoparticles are not available, which are also size and temperature dependent,[21] we cannot quantitatively estimate the thermal expansion coefficient. Qualitatively, however, from Eq. (3), we can know the coefficient of lattice thermal expansion for silver nanoparticles in vacuum is smaller than that of bulk silver due to surface tension.

When Ag nanoparticles are exposed to ambient air, gas molecules will adsorb onto the surface of the particles. For instance: at room temperature, oxygen O_2 in contact with silver can undergo the two following reactions:[22]

$$Ag + O_2 \rightarrow Ag^{+}O^{-}_{2(\mathrm{ads})},$$

$$4Ag + O_2 \rightarrow 4Ag^{+} + 2O^{2-}_{\mathrm{ads}}, \qquad (4)$$

i.e., chemisorption of O_2 in air will occur on the surface of metal Ag. The Ag nanoparticles dispersed within pores of mesoporous silica are in contact with ambient air and hence with the oxygen in air. It is expected that the chemisorption will take place at lower temperature. Obviously, oxygen adsorption will decrease surface energy of Ag nanoparticles significantly. Such decrease will induce lattice expansion and rise of thermal expansion coefficient relative to the particles in vacuum based on Eqs. (1) and (3), which is qualitatively in agreement with our experimental results (see Fig. 2). However, the adsorbed oxygen will desorb at higher temperature. On the other hand, when Ag is exposed to ambient air, oxygen in air will dissolve into the Ag lattice, especially at high temperature, because the solubility will increase with rising temperature.[23] Outlaw *et al.*[24] found that atomic oxygen can dissolve preferentially into the octahedral interstitials of the silver lattice. Nagy *et al.*[25] *in situ* measured XRD spectra of bulk silver in pure oxygen and ethanol–argon mixture gas, respectively, and found that exposure to oxygen induces lattice expansion, which is caused by oxygen dissolution in the lattice, while exposure to the ethanol–argon mixture shows no detectable change of lattice constant. In our case, oxygen in air will enter into the lattice of Ag nanoparticles at high temperature and induce additional lattice expansion. The oxygen dissolved in Ag lattice is difficult to escape in subsequent treatments in vacuum, and hence the diffraction peak cannot return to the original position [see curves (a) and (c) in Fig. 3] (the chemical adsorption of oxygen should be relatively negligible at 700 °C). In a word, both oxygen adsorption on the surface and dissolution in the lattice induce lattice expansion compared with the particles in vacuum. Obviously, the former should be dominant at lower temperature, and at higher temperature the latter is dominant.

As for the possible effect from the silica support, it should be negligible compared to the oxygen atmosphere and the particles' surface tension, because the silica is a weak interacting medium with Ag.[1] Although the thermal expansion of free-standing Ag nanoparticles cannot be measured by XRD, we believe that the results would be very similar to those of Ag nanoparticles dispersed within silica.

In summary, we have reported a study of thermal expansion behavior for Ag nanoparticles in air and vacuum in the temperature range of 25–700 °C, by dispersion of the particles within pores of mesoporous silica and *in situ* XRD measurement. The thermal expansion coefficient of Ag nanoparticles in vacuum is much smaller than that of bulk Ag, only about one fourth of the latter, due to surface effect of the particles. However, the coefficient in air is about 3 times as high as that in vacuum and close to the value of bulk Ag because of oxygen adsorption on particles' surface and dissolution into the lattice. This study could be of importance not only in fundamental academic interest, but also in the structural design, thermal stability, and reliability of future nanodevices.

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