

Carrier mobility of iron oxide nanoparticles supported on ferroelectrics studied by Mössbauer spectroscopy

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Abstract ^{57}Fe Mössbauer spectroscopy was performed on two types of Fe oxide nanoparticles supported on a typical ferroelectric, BaTiO_3 . It was found that the valence state of FeO nanoparticles changed to a mixed $2+/3+$ state at high temperature where BaTiO_3 shows paraelectric behaviour. We attribute this phenomenon to the fluctuation of electric dipoles which realizes carrier injection into the Fe oxides. This is the first report which discusses a dynamical valence state of transition metal oxides supported on ferroelectrics.

Keywords Ferroelectric · Electric dipole · Nanoparticles · Mössbauer spectroscopy

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1 Introduction

Valence instability of transition metals is a key element in the modern material science since it is responsible for charge ordering phenomena [1], metal-insulator transitions and even a superconducting transition from a metallic oxide conductor. Our motivation for this study is the search for such valence instability in an artificial junction between a transition metal and ferroelectric material. A typical characteristic of ferroelectrics is the existence of a spontaneous polarization originating from long range ordering of electric dipoles [2]. And it transforms into a paraelectric phase above the ferroelectric transition temperature, T_c , where the electric dipoles are fluctuating with a pico- to nanosecond time interval, with a short coherence length.

We have investigated the valence state of metallic nanoparticles supported on paraelectric materials because the surface of the paraelectric is expected to have a high frequency electric potential variation. Such high frequency fluctuation of the electric potential on the surface of the paraelectric may cause some unusual effects to adhering metals. Recently, we found a new morphology in the interface between Pb nanoparticles and a ferroelectric [3]. Pb nanoparticles supported on a ferroelectric $\text{Pb}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ (PST) show a stable metallic surface in the ambient air. During the investigation of the un-oxidized state of Pb particles on PST, our research was focusing on the valence state investigation of the nanometals supported on some paraelectric materials.

It has been generally understood that ferroelectrics are typical wide band-gap insulating materials without any free carriers in the bulk system. But recently, electronic conduction at the ferroelectric domain wall of BiFeO_3 and high carrier mobility owing to the electron gas at the cleaved surface of SrTiO_3 has been found [4, 5]. If the polarization fluctuation of the ferroelectric or the paraelectric state can drive some conduction carriers into the adhered transition metal material, it may provide a new functionality.

Among such transition metal elements, Fe is the most ubiquitous and useful material for actual applications. If the nano-sized Fe composite on the ferroelectric shows a new and nonequilibrium state, it may start to develop some novel functionality. For the investigation of the valence state and the particle character of Fe nanocompounds supported on ferroelectrics, Mössbauer spectroscopy is the best method to obtain the rich information. In this study, we report on the valence state and the particle size of two types of Fe nanocompounds supported on the typical ferroelectric, BaTiO_3 particles.

2 Experimental

Fe_2O_3 nanoparticles were purchased from Nano cube Japan Co., Ltd. The particles are dispersed in urea (2 wt% Fe in urea), and the particle size is uniformly 3 nm. FeO nanoparticles were purchased from Quantum Sphere, Inc. The particle size is approximately 20 nm. These nanoparticles have a core shell structure where the core is metal Fe and the shell is FeO. BaTiO_3 with particle diameter of 100 nm was purchased from Toda Co., Ltd.

The sample preparation procedure is as follows. Fe_2O_3 nanoparticles supported on BaTiO_3 (10 wt% $\text{Fe}_2\text{O}_3/\text{BaTiO}_3$) were fabricated by rotary kiln in reducing

atmosphere. First, 14.3 g of urea solution in which 2 wt% FeO nanoparticles are dispersed and 2.0 g of BaTiO₃ was added to 50 g of ethanol, then irradiated by ultrasonic wave and dispersed well. Then the ethanol was evaporated at 300 °C and the sample was heated at 600 °C for 1 h in 10⁻⁶ atom O₂/Ar in a quartz glass vessel rotating at 60 rpm. The sample was then let to cool down spontaneously to room temperature in 10⁻⁶ atom O₂/Ar. FeO nanoparticles supported on BaTiO₃ (10 wt% FeO/BaTiO₃) were also prepared by rotary kiln in reducing atmosphere. First, 0.204 g of FeO nanoparticles and 2.0 g of BaTiO₃ were put into a quartz glass vessel, then the vessel was annealed at 1000 °C for 2 h in 10 % H₂/Ar mixture gas rotating at 60 rpm and let to cool down to room temperature spontaneously.

The morphology was characterized by a 200 kV transmission electron microscope (TEM) of JEOL 2100F equipped with a scanning electron microscope (SEM) system. X-ray diffraction (XRD) was used in order to characterize the crystal structures. Small peaks originating from Fe were apparent but the crystal structures could not be identified, because the content of Fe was too low and Fe oxides particles were too small. So we used ⁵⁷Fe Mössbauer spectroscopy which was conducted in conventional transmission geometry by using ⁵⁷Co-in-Rh (25 mCi) as the γ ray source [6]. The powder type sample was set in a vacuum furnace for the high temperature measurements (10⁻² Torr, up to 773 K) or in a closed cycled cryostat for the low temperature measurements.

3 Result and discussion

Figure 1 displays the bright field image of the products measured by TEM. Fe₂O₃ and FeO nanoparticles were successfully deposited on ferroelectric BaTiO₃: the average diameter of Fe₂O₃ and FeO nano-particles are 10 nm and 40 nm, respectively. Fe₂O₃ nanoparticles have a size distribution from 5 to 15 nm and are uniformly dispersed on the BaTiO₃ particle. In the case of FeO, almost all particles have a size of 40 nm. At the same time, small nanoparticles with an estimated size of 5 nm were partially supported on BaTiO₃.

Figure 2a shows the temperature dependence of Mössbauer spectra measured in Fe₂O₃/BaTiO₃. The spectrum measured at 285 K consists of a clear doublet and traces of a broad sextet. The doublet has an isomer shift of 0.35 mm/s indicating that the valence state of Fe is 3+. When decreasing the temperature to 16 K, the spectrum exhibits only a sextet. This feature is a result of superparamagnetic behavior of Fe₂O₃ particles [7]. This indicates that the diameter of the Fe₂O₃ particles is several nanometer, in agreement with the diameter of Fe oxide particles observed in TEM images. In the higher temperature measurement, the peaks originating from superparamagnetic contributions remain, indicating that Fe₂O₃ nanoparticles do not grow in size.

Figure 2b displays the temperature dependence of Mössbauer spectra measured in FeO/BaTiO₃. The Mössbauer spectrum at 291 K shows both a doublet and traces of a sextet apparently similar to the case of Fe₂O₃/BaTiO₃. The doublet, however, has an isomer shift of 0.935 mm/s and a quadrupole splitting of 0.760 mm/s, which indicates that the Fe ions are in the high spin Fe²⁺ state. Fe²⁺ may exist as FeO, Fe₂TiO₄, FeTiO₃, or superparamagnetic Fe²⁺ oxides. But considering the spectra at low temperatures, the doublet is attributed to FeO, whereas the sextet peaks indicate

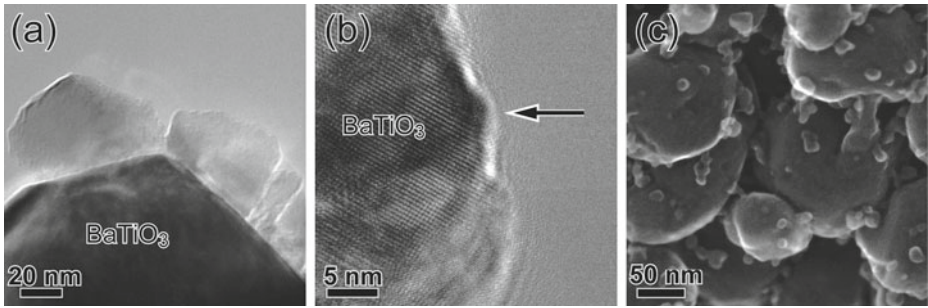


Fig. 1 Bright field image **a**, high-resolution image **b** of 10 wt% FeO/BaTiO₃ and SEM image **c** of Fe₂O₃/BaTiO₃. In **b**, arrow indicates small Fe oxide nanoparticles with a size of 5 nm

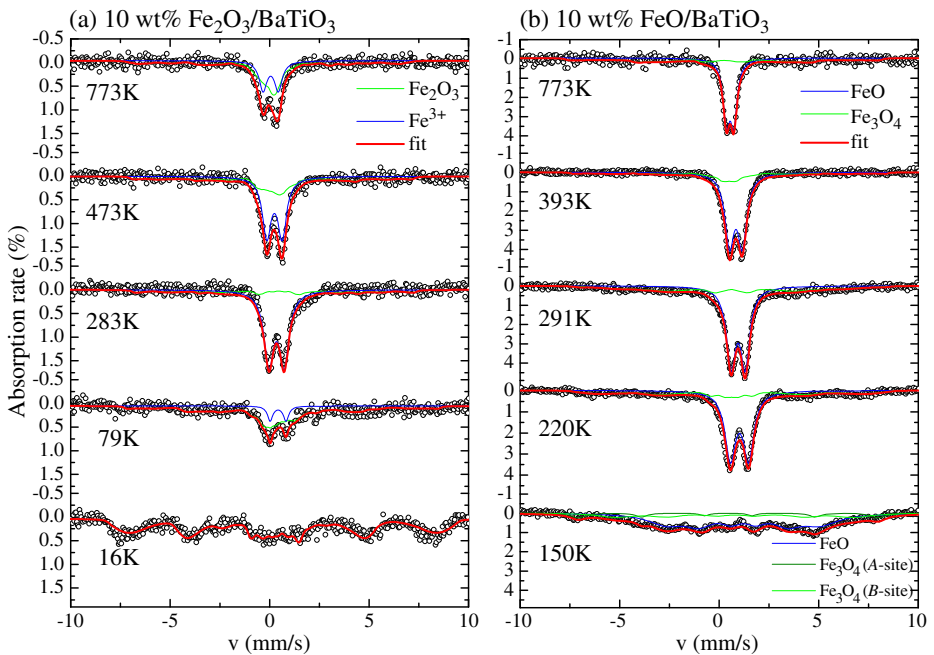
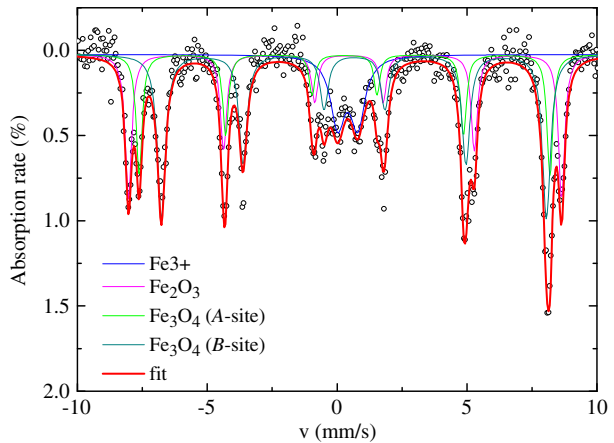


Fig. 2 Mössbauer spectra of 10 wt% Fe₂O₃/BaTiO₃ **a** and 10 wt% FeO/BaTiO₃ **b** at various temperatures. Color solid lines are the fitted curves

superparamagnetic Fe₃O₄. The TEM measurement of FeO/BaTiO₃ indicated that Fe oxide nanoparticles have two types of size. One is a diameter of 30 nm, corresponding to FeO. Other smaller particles have a diameter of 3 nm, corresponding to Fe₃O₄. In the high temperature region above room temperature, the value of the quadrupole splitting of the doublet decreases. This is normal for high spin Fe²⁺. On the other hand, the sextet becomes sharper and its hyperfine field increases with increasing temperature. This suggests that Fe₃O₄ nanoparticles become enlarged. To check the stabilization of Fe oxides on BaTiO₃, the sample was annealed at 773 K in 10⁻² Torr

Fig. 3 Mössbauer spectrum of 10 wt% FeO/BaTiO₃ annealed at 773 K for 10 h. This data were recorded at 289 K after cooling from 773 K. Color solid lines are the fitted curves



O₂ atmosphere for 10 h. The spectrum measured at 289 K after the annealing is shown in Fig. 3. It is seen that the doublet corresponding to FeO disappeared and changed to other sextet spectra. This result indicates that FeO is oxidized and changes to Fe₂O₃ or Fe₃O₄.

We remark that this change is unusual because FeO is normally stable under the thermodynamic condition where the sample was heated at 773 K in 10⁻² Torr O₂ atmosphere for 10 h. On the other hand, the Fe₃O₄ nanoparticles with 5 nm size show only a weak particle growth and the valence of Fe was not changed. It means that the annealed particle remains in a stable condition because the particle growth occurs with local evaporation and rearrangement of Fe and O. We suppose that this unusual behavior can be attributed to re-aggregation of Fe and O affected by the BaTiO₃ surface. It is well known that BaTiO₃ shows a paraelectric phase above 403 K. In the paraelectric phase, the spontaneous polarization is melted and the electric dipoles are fluctuating with short range coherence. It causes local fluctuation of the electric charge density. It is known that the energy band gap changes approximate 0.3 eV between the ferroelectric phase and paraelectric phase [8]. So it is considered that the fluctuation of the electric charge density with the short range coherence causes the fluctuation of 0.3 eV in electrical potential.

Note that in the reduction annealing process, BaTiO₃ has an oxygen defect band under the conduction band minimum. It is considered that the Fe oxides and BaTiO₃ are band-aligned at their Fermi level, and at the same time the fluctuation of electric potential of Fe and that of the electric dipoles in BaTiO₃ are synchronized with the pico to nano second time interval. This band structure leads to the instability of the Fe valence. When FeO nanoparticles are re-aggregated after decomposition at high temperature annealing, the Fe valence is not stabilized to 3+ but fluctuates in a 2+/3+ mixed state. On the other hand, in the case of Fe₂O₃/BaTiO₃, particle growth and valence instability did not occur. This implies that the evaporation and rearrangement of Fe ion and O ion is hard to occur and grain growth is also hard to occur in the stable crystal structure, compared with the unstable crystal structure.

4 Conclusions

We report Mössbauer spectroscopy experiments in which we observe the dynamics of the Fe valence state affected by a ferroelectric surface. Fe_2O_3 or FeO nanoparticles supported on ferroelectric BaTiO_3 particles shows a thermodynamically instable Fe valence state. We assume that the electric dipole fluctuation of the paraelectric phase of the ferroelectric plays an essential role in the valence instability of the Fe atom. One possible mechanism to explain the valence instability is that the fluctuation of electric dipoles gives rise to a the continuous carrier injection into the Fe compounds. This result provides a new research area of applications using the paraelectric property.

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