Magnetism of Undoped ZrO₂ Nanoparticles Deposited by Plasma-Gas-Condensation Technology

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Abstract. The magnetic properties of undoped ZrO₂ nanoparticles (NPs) deposited by plasma-gas-condensation technology were studied. The as-prepared ZrO₂ NPs with controllable particle sizes (6-13 nm) presents tetragonal phase which was hardly acquired by traditional methods at room temperature. The as-deposited ZrO₂ NPs were annealed at 300 to 1000 °C in air or mixed gas of Ar (95%) + H₂ (5%) for 3 h, respectively. XRD results show that the phase of ZrO₂ NPs gradually transformed from tetragonal to monoclinic with increasing the annealing temperature. The magnetic results of ZrO₂ NPs under all annealing treatments were paramagnetic, which are different with the diamagnetic or ferromagnetic ones, also different from magnetic property changed after annealing in some other works.

1. Introduction
Although unanticipated room-temperature ferromagnetism was found in many nonmagnetic metal oxide nanostructural materials without any doping [1-10], the origin of ferromagnetism still maintained debatable. Thanks to the wide band gap, thermally stability and high dielectric constant [11], ZrO₂ has a promising future in spintronics material and was being studied as the gate-dielectric in field effect transistors [12, 13]. Therefore, studying on the magnetic properties of undoped ZrO₂ is of great academic and practical significance.

Due to the possible undetected ferromagnetic impurities, the controversy in the ferromagnetism of nonmagnetic metal oxide nanostructural materials mainly embodied on whether the ferromagnetic was intrinsic [14-16]. For example, Hadacek et al. [14] and Abraham et al. [15] consider that ferromagnetism in such materials arise from the ferromagnetism impurity contamination. However, the coercivity detected in such materials is too small to distinguish the ferromagnetic is intrinsic or extrinsic. Meanwhile, creation mechanism of this ferromagnetism in such undoped materials was diversiform without a consensus. For example, Rao et al. [3, 6] consider that the exchange interactions of unpaired electron spins resulting from superficial oxygen vacancies generate the ferromagnetism. Coey et al. [1, 2] consider that the necessary ferromagnetic coupling is obtained from the polarized impurity band formed by defect-related electrons. Sanvito et al. [5] and Gallego et al. [17] consider that cation vacancy is the origin of this ferromagnetism by means of ab initio calculation. Therefore, for clarifying the origin of ferromagnetism in undoped nonmagnetic metal oxide nanostructural materials, a preparation method which can synthesize high purity nanosacle samples and systematically study on effects of defect on magnetic properties of such materials are necessary.

In this work, the plasma-gas-condensation technology [18] was used to synthesize ZrO₂ nanoparticles with uniform morphology and controllable particle diameters. The as-prepared undoped ZrO₂ NPs are surface clean and contamination free thanks to the vacuum condition and organic-free in
the gas-phase synthesis process. Therefore, the preparation method in our work is very suitable for studying the magnetic properties of such undoped nonmagnetic metal oxide nanostructural materials because the impurity interference can be ignored. In this work, we not only ensure the purity of samples in preparation but also focus on all possible pollution in handling or measurement procedures, especially ensure that there is no contamination on account of using iron based tools in any step of sample processing. As done by many studies, systematic and various annealing treatment were applied to our ZrO$_2$ NPs for observing changes of magnetic properties.

2. Experimental

2.1. Deposition of ZrO$_2$ Nanoparticles
During the process of gas-phase synthesis, high density Zr vapor was produced by two Zr targets (99.99%) fixed oppositely with a dc sputtering source. For obtaining nanoparticles with various morphology, the different Ar gas flow rate were imported into sputtering chamber with the fixed sputtering current 0.8 A. The sputtered Zr atoms nucleated and grew by colliding each other and then flew into deposition chamber, finally landed onto the substrates and grew into nanoparticles. The deposition rate of ZrO$_2$ nanoparticles was measured by the quartz oscillator thickness monitor. The equivalent thickness of ZrO$_2$ particles assembling films can be estimated by the deposition time and deposition rate. The Zr nanoparticles with controllable sizes were obtained by changing the flow rate of Ar gas. Due to high surface activity, the as-prepared Zr NPs at initial deposition stage completely oxidized to tetragonal ZrO$_2$ when removed from the deposition device. For studying the magnetic performance of ZrO$_2$ NPs with different crystal structure and defect concentration, the as-deposited samples were annealed at 300 to 1000 $^\circ$C in air and mixed gas of Ar(95%)+H$_2$(5%) for 3 h, respectively.

2.2. Measurement of ZrO$_2$ NPs Properties
Transmission electron microscopy (TEM) of JEOL-2100 was employed to studied ZrO$_2$ NPs with thickness of about 2 nm deposited on TEM copper grids. Surface morphology of NPs with thickness of 400 nm was tested by scanning electron microscope (SEM) LEO-1530FE. The crystalline structures of ZrO$_2$ NPs on quartz glasses before and after annealing were investigated by a Panalytical X’pert PRO X-ray diffractometer. The MPMS was used to investigate the magnetic hysteresis loops of ZrO$_2$ NPs with effective thickness of about 400 nm at 5K.

3. Results and Discussion
The TEM images of ZrO$_2$ NPs prepared with Ar gas flow rate of 200 to 500 sccm deposited on TEM copper grids with effective thickness about 2 nm are shown in Figure 1(a). The corresponding statistical results of size distribution and average particle diameter ($d$) estimated by image-analysis software are shown in Figure 1(b). It can be seen that ZrO$_2$ NPs prepared at different $R_{Ar}$ had a narrow size distribution and the average diameters were controlled between 6.3 to 12.7 nm. The average particle diameter $d$ increases with increasing the flow rate of $R_{Ar}$. In the synthesis process, Ar gas is used as sputtering and condensation gas at the same time. As the increasing of $R_{Ar}$, quantity of Zr vapor and Zr-Ar collision probability increases and then the growth of ZrO$_2$ NPs are promoted. If the ZrO$_2$ NPs continuously deposited onto the silicon, the nanoparticles assembling films were obtained. It can be seen from the SEM image (Figure 2) that ZrO$_2$ nanoparticles-assembled thin films deposited on Si wafer with effective of about 400 nm are accumulated continually by lots of tiny ZrO$_2$ particles.
Figure 1. The TEM Images (a) and Corresponding Size Distribution (b) of ZrO$_2$ Nanoparticles Obtained with Different $R_{\text{Ar}}$

Figure 2. SEM Image of ZrO$_2$ NPs Assembling Films with Effective Thickness of 400 nm Prepared at $R_{\text{Ar}} = 200$ sccm and I = 0.8 A.

Figure 3(a) presents the XRD pattern of as-prepared ZrO$_2$ NPs ($d = 6.3$ nm) deposited on glass with thickness of 400 nm. Compared with the pattern of pure quartz glass (blue line in Figure 3(a)), the ZrO$_2$ emerges the peak of tetragonal ZrO$_2$ (101) crystal plane. Because of small size, high defect concentration and poor crystallinity the diffraction peak broadens seriously, but this condition can be improved well by annealing. In normal case, bulk ZrO$_2$ is stable with monoclinic phase instead of tetragonal phase below 1170 °C under normal atmospheric conditions [19]. Owing to dimension effect, the as-prepared ZrO$_2$ NPs possess high defect concentration and surface energy. For reducing the system energy of NPs, ZrO$_2$ revealed the high temperature phase (tetragonal) at ambient pressures and temperatures [20-23]. Thus, the undoped tetragonal ZrO$_2$ which was difficult to obtain at room temperature via traditional synthetic methods can be synthesized by plasma-gas-condensation. Figure 3(b) shows the magnetization curve of ZrO$_2$ NPs on Si substrate. It can be seen that pure Si substrate reveals obvious diamagnetic (red line in Figure 3(b)). After eliminating the diamagnetic signal of Si substrate, the magnetization curve of as-prepared ZrO$_2$ NPs is almost linear. This indicates that the tetragonal ZrO$_2$ NPs with average diameter of 6.3 nm is paramagnetic. This result is not in agreement with ferromagnetism [1-10] or diamagnetism [15] found by many similar studies.

In the study of diluted magnetic oxides, the magnetic properties are closely related to the crystal
structure and defects [5, 24]. According some reports, the ferromagnetism nanoscale HfO$_2$ or ZrO$_2$ usually present monoclinic phase [2] rather than tetragonal phase in our ZrO$_2$ NPs. Therefore, for studying the effects of crystal structure, crystallinity and oxygen vacancy on magnetic properties, as-prepared ZrO$_2$ NPs were annealed in air from 300 to 1000 °C for 3 h, respectively. The XRD patterns of ZrO$_2$ NPs annealed with various temperatures are shown in Figure 3(c). This indicated that the crystallinity of tetragonal ZrO$_2$ NPs was greatly improved as annealing temperature increased. At the annealing temperature of 800 °C, ZrO$_2$ NPs still maintain tetragonal phase so that the pure tetragonal ZrO$_2$ at low temperature can be study by plasma-gas-condensation technology. After annealing at 1000 °C in air for 3 h, part of ZrO$_2$ transformed into monoclinic phase from tetragonal phase. The corresponding magnetic properties of ZrO$_2$ NPs annealed at various temperatures in air were measured by SQUID at 5 K (Figure 3(d)). All the magnetic results indicate that ZrO$_2$ NPs are paramagnetic after all annealing treatments despite it is tetragonal or monoclinic phase, poor or good crystallinity. Furthermore, defect concentration especially oxygen vacancy decreased with the increase of annealing temperature in air (oxidizing atmosphere). Therefore, air-annealing couldn’t change the magnetic property of ZrO$_2$ NPs which is not in agreement with some similar studies [1, 4, 7, 8, 25].

Some researchers also consider that for achieving ferromagnetism in nanoscale oxide, the vacancy concentration of the system should be high [26-28]. For further study on effects of high oxygen vacancy on magnetic properties, ZrO$_2$ NPs were annealed in reducing atmosphere (mixed gas of Ar(95%) and H$_2$(5%)) from 300 to 1000 °C for 3 h, respectively. A similar XRD results are shown in Figure 3(e). As annealing temperature increased, crystallinity of tetragonal ZrO$_2$ NPs was greatly improved and transformed into monoclinic phase at the annealing temperature of 1000 °C. Figure 3(f) shows the corresponding magnetization curves. It can be seen that the magnetic properties still maintain paramagnetic although the paramagnetic moment decreased slightly. Therefore, the increasing oxygen vacancy obtained by annealing in reducing atmosphere couldn’t change paramagnetic result to ferromagnetism.

Figure 3. (a) XRD patterns and (b) magnetization curves of as-prepared ZrO$_2$ NPs deposited on quartz glass and pure Si substrates, respectively. (c) XRD patterns and (d) magnetization curves of ZrO$_2$ NPs before and after annealing in air atmosphere for 3 h at various temperatures, respectively. (e) XRD patterns and (f) magnetization curves of ZrO$_2$ NPs before and after annealing in mixed gas of Ar (95%) and H$_2$ (5%) for 3 h at various temperatures, respectively.
As described above, the ZrO₂ NPs with effective thickness of 400 nm and average diameter of 6.3 nm deposited on Si substrate presents paramagnetic instead of diamagnetism or ferromagnetism reported in recent research. Similar paramagnetic behavior has also been found in HfO₂ by Tirosh et al. [25] and copper-doped ZrO₂ by Dutta et al. [29], in which this result was regarded as defect or vacancy related. The extended defects might create delocalized and spin-polarized states and then generate magnetic moment [30]. As a result of size-effect, there is a large aggregate superficial area and defect concentration in ZrO₂ nanoparticles. Therefore, we think that the observed paramagnetic behavior in ZrO₂ NPs should be also defect related. However, the paramagnetic result rather than ferromagnetism might be because magnetic properties of undoped nonmagnetic metal oxide nanostructural materials are related with their preparation method, and ferromagnetic results might have stringent demands on morphology, defect types, defect concentration and distribution in such nanostructural materials.

The paramagnetic was maintained even when crystal structure, crystallinity and oxygen vacancy concentration changed after annealing at different temperatures and atmosphere (see Figure 3). This indicates that the paramagnetic of undoped ZrO₂ NPs prepared by plasma-gas-condensation method is stable and rarely affected by the change of crystal structure, crystallinity and oxygen vacancy concentration. This is not the same with magnetism changed from ferromagnetic or paramagnetic to antiferromagnetic after annealing treatments detected by Coey and Tirosh [1, 25], respectively. Therefore, further work on the clarification of the diamagnetic behavior in such nanoscale material synthesized by gas-phase method is underway.

4. Conclusions
In our work, tetragonal ZrO₂ nanoparticles with uniform morphology and controllable particle diameters (6-13 nm) through modifying the flow rate of Ar gas were prepared by plasma-gas-condensation technology. After annealing at different temperatures in oxidizing or reducing atmosphere for 3h, respectively, tetragonal ZrO₂ partly converted into monoclinic phase at the annealing temperature of 1000 °C and their magnetic properties remained paramagnetic despite the change of crystal structure, crystallinity and oxygen vacancy concentration. The paramagnetic result in our work is different with the ferromagnetic or diamagnetic one, also different from magnetic property changed after annealing treatments in some reports. However, whether this experimental phenomenon also applies to every such nanoscaled materials with different morphologies and dimensions, this interesting result provides a new experimental phenomenon and basis for the study on magnetic properties of undoped nonmagnetic metal oxide materials.

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6. References
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