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Synthesis and magnetic properties of ceramic MgO porous film

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ABSTRACT

Ordered porous MgO films with pore diameters in the 15–28 nm range have been prepared on porous anodic alumina substrates at 573 K in a fixed O_2 pressure of 1.4×10^{-4} mbar using DC-reactive magnetron sputtering. X-ray diffraction and scanning probe microscope observations have revealed that homogeneous MgO ceramics with face-centered cubic structure are formed with a highly ordered nanopore array arranged in a close packed hexagonal pattern. The results of magnetic measurements have shown that the porous MgO ceramics possess remarkable room temperature ferromagnetism and the maximum saturation magnetization along the out-of-plane direction was as high as 78 emu/cm^3. Experimental and theoretical results suggest that oxygen vacancies and the unique porous structure of the films are responsible for the high magnetization. These results provide new insights into magnetic ordering in undoped dilute ferromagnetic semiconductor oxides and may be useful in the development of MgO-based spintronics devices and novel multifunctional materials.

1. Introduction

In recent years, the ferromagnetism induced by lattice defects or nonmagnetic impurities termed d^0 ferromagnetism has attracted great interests in the field of spintronics [1–3]. MgO is a typical d^0 oxide for investigating d^0 ferromagnetism due to its exceptional properties, such as extraordinary stability, low thermal conductivity and high secondary electron emission yield, et al. [4–7]. Recently, room temperature ferromagnetism (RTFM) has been reported in MgO nanoparticles and films due to the presence of point defects, which opens new possibilities for spin photonic device application [8–10]. However, the magnetic property found in these materials is rather weak as their saturation magnetizations are usually only a few emu per cubic centimeter, thus limits their practical application [11–13]. Though there is a consensus that native defects play a crucial role in inducing ferromagnetism, considerable controversies on the intrinsic nature of the unexpected ferromagnetism still exists since conventional ideas of magnetism are unable to account for the ferromagnetism. By taking ab initio calculations based on the density functional theory, Gao et al. proposed that above a critical concentration (6.25%) of Mg vacancies could convert the MgO insulator to half-metal [14]. Additionally, Zhang et al. predicted that local magnetic moment could be induced by the composite defects around the oxygen vacancy [15]. Experimentally, Kumar suggested the origin of magnetic moment in MgO nanoparticles is due to Mg related vacancies at the surface of the particles [16]. Furthermore, it is investigated that MgO thin films prepared by pulsed laser deposition technique exhibit ferromagnetism due to the Mg vacancies [13]. Nevertheless, cation vacancies induced RTFM order was later put into question as the MgO nanocrystallites exhibited reduced magnetic spin-order after air annealing, which in turn demonstrates that oxygen vacancies play a crucial role in percolation of RTFM spin order [17]. Although there are many theoretical and experimental studies regarding RTFM in MgO, there is no a consistent conclusion about the specific mechanism. The main cause of this phenomenon is because the room temperature ferromagnetism in MgO thin film is too weak. Therefore, it is worthy of further research to find out how defects induce the RTFM of undoped MgO films and how to devise ways to improve this RTFM.

In this work, direct current (DC) reactive magnetron sputtering technique is utilized to fabricated MgO films on porous anodic alumina (PAA) substrates, which is ideally suited for the introduction of large defect concentrations. Experimental results show that large room temperature ferromagnetism can be obtained in the direction perpendicular to the plane of the MgO films. The mechanism of ferromagnetism in MgO films is specifically discussed. The results suggest that the introduction of large specific surface area and oxygen vacancy defects may offer an effective way to bring magnetic moments in various non-magnetic materials.

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2. Experimental

Magnesium oxide ceramics were deposited by DC-reactive magnetron sputtering technique on PAA substrates using pure magnesium target (99.995%) in presence of high purity argon and oxygen ambience at 573 K. The oxygen partial pressure 1.4×10^{-4} mbar was maintained in the chamber with a total pressure of 3×10^{-3} mbar. The deposition time *t* was kept at 1 h, 2 h, and 3 h, respectively and the corresponding sputtering power was 60 W. Care was taken to keep the samples away from any magnetic contamination in the whole process.

The PAA substrates were prepared by a two-step anodic oxidation process in 0.3 M oxalic acid under a constant DC voltage (45 V) [18].

The structural properties of ceramic MgO thin films were investigated by X-ray diffractometer (XRD) with Cu K_α radiation, whereas the morphological studies were characterized using field-emission scanning electron microscope (FE-SEM. Hitachi S-4800) and a scanning probe microscope (SPM, Veeco Nanoscope IV). The elemental composition of the films was verified using energy dispersive spectroscopy (EDS) system operated at 20 KV. The magnetic behavior of the films was measured with vibrating sample magnetometer in Physical Properties Measurement System (PPMS-6700) and a superconducting quantum interference device (SQUID) from Quantum Design. The photoluminescence (PL) spectrum was obtained on a Shimadzu RF-5301PC fluorescence spectrophotometer under an excitation of the 340 nm line of a Xe lamp.

3. Results and discussions

The XRD pattern and SPM images about MgO thin films deposited for 2 h are shown in Fig. 1. The peak at about 42.9° corresponding to (200) of cubic MgO is clearly visible in XRD pattern and no other impurity phase is detected within the detection limits. EDS result shows that the sample consists of O, Mg and Al element, corresponding to 65.06%, 4.84% and 30.10% of atom percentage, respectively, from which one can clearly see that the sample is mainly MgO and the signals of Al and some of O come from the PAA substrates, ruling out the incorporation of any additional magnetic impurities in the thin films. In addition, surface atomic structure and the corresponding the three dimensional (3-D) surface topographies were examined for the MgO film using scanning probe microscope with a scanning area of 1 μm × 1 μm. As can be seen from Fig. 1(b), a highly ordered nanopore array

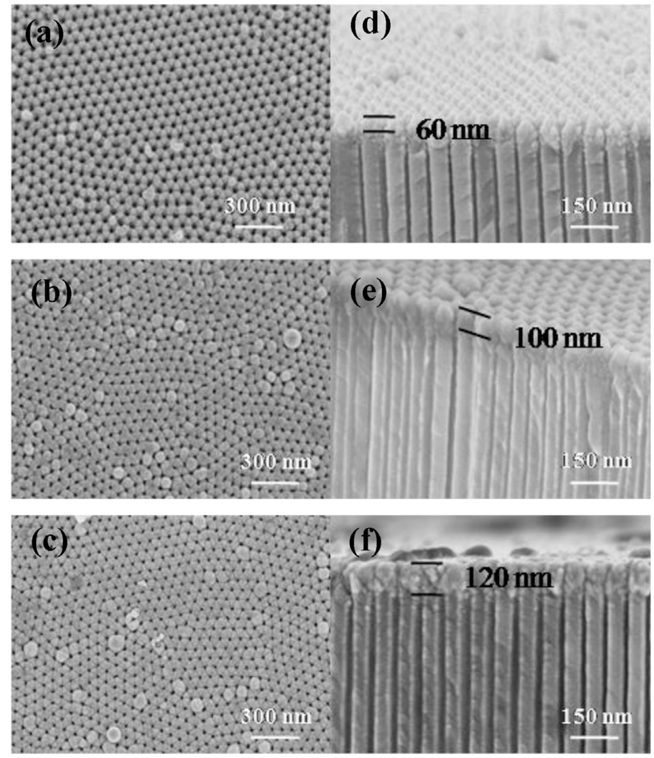

Fig. 2. The left images are surface SEM images of MgO thin films deposited with different sputtering times. (a) 1 h (b) 2 h and (c) 3 h. The right images of (d), (e) and (f) are the corresponding cross section of the samples.

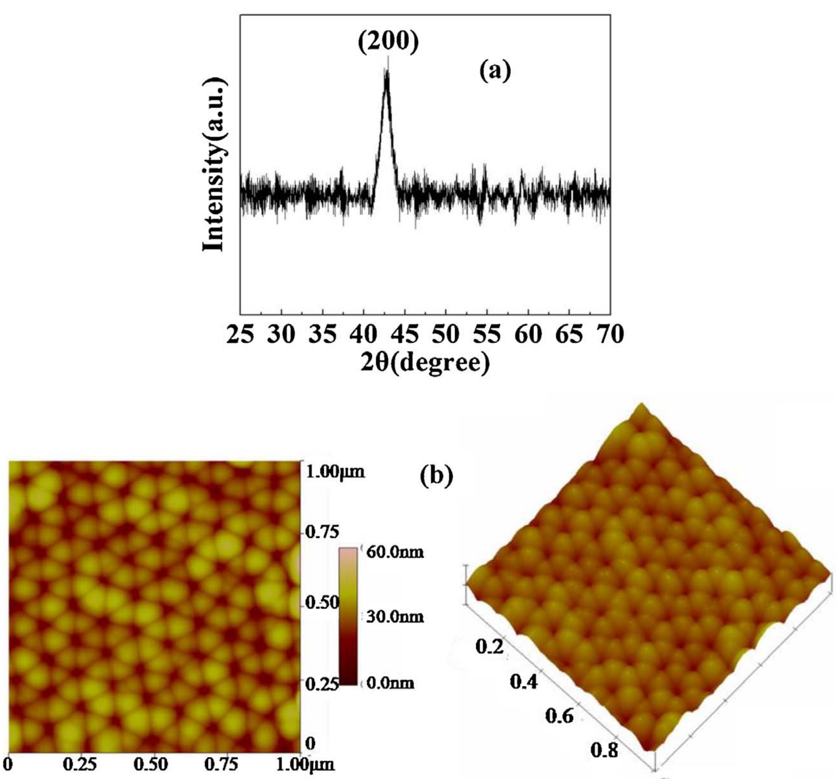

Fig. 1. The (a) XRD pattern and (b) surface atomic structure and the corresponding 3-D surface topography for the MgO films deposited for 2 h.