Defect-Induced Ferromagnetism with T_c Higher than Room Temperature in CaO Films

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Received date: 2021-03-04; accepted date: 2021-05-15

【Abstract】 We successfully prepared CaO thin films on the (111)-oriented yttrium-stabilized zirconia (YSZ) substrates by a pulsed laser deposition (PLD) technique. The intrinsic nature of ferromagnetism in CaO films has been established with the experimental observation of the magnetic hysteresis loop at room temperature. The X-ray diffraction and X-ray photoelectron spectroscopy analysis have shown that the prepared CaO films are (111)-oriented and no impurity phases are detected. The CaO films were grown and annealed under high vacuum conditions always exhibit magnetization signal, which was not detected in its corresponding target. It is found that there are correlations between the vacancy concentration and the magnetization of CaO films, which suggests that the oxygen vacancy concentration is directly related to the ferromagnetism.

Keywords: pulsed laser deposition; CaO thin film; oxygen defect; ferromagnetism

PACS: 6110,7360F,8115I

DOI: 10.13380/j.ltpl.2021.01.004

Reference method: HE Wenlan, WANG Qiongpei, XU Liqiang, WANG Lingfei, LI Guang, Low. Temp. Phys. Lett. **43**, 0033 (2021)

氧化钙薄膜中缺陷诱导的高居里温度铁磁性研究

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收稿日期:2021-03-04;接收日期:2021-05-15

【摘要】 通过脉冲激光沉积在(111)取向钇稳定的氧化锆(YSZ)衬底上制备了氧化钙(CaO)薄膜.室温

* 安徽文达信息工程学院重点项目:钙钛矿型氧化物的制备及氧含量、磁场调控(XZR2020A05);基于FPGA的多摄像头视频采集系统(XZR2019A12);互联网+医院应用研究(XZR2018A14);2020年高校优秀青年骨干教师国内访问研修项目,项目编号(gxgnfx2020125);2020年安徽省省级质量工程自动化专业实践教学体系研究项目,项目编号(2020jyxm0770)资助的课题.

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下磁滞回线的实验观测数据表明 CaO 薄膜具有明显的铁磁性. X 射线衍射和 X 射线光电子能谱分析表明,CaO 薄膜为(111)取向,没有杂质相. 在高真空条件下生长和退火的 CaO 薄膜都表现出铁磁性磁化行为,而在相应的 CaO 靶材上没有检测到这种铁磁性. 结果表明,氧空位浓度与氧化钙薄膜的磁化强度之间存在一定的相关性,后退火对 CaO 薄膜磁性的影响说明,氧空位浓度与氧化钙薄膜的铁磁性是相关的.

关键词: 脉冲激光沉积;CaO 薄膜;氧缺陷;铁磁性

PACS: 6110,7360F,8115I

DOI: 10.13380/j.ltpl.2021.01.004

1 Introduction

Oxide materials have been one of the most attractive research topics in physics and materials science, e. g. , binary oxide and double and layered perovskites. Recently, the transition metal doped semiconductors, such as ZnO and TiO_2, have revealed many novel and exciting phenomena and challenged our view of the solid-state physics.

Pure Calcium oxide (CaO) has a rock salt structure with a lattice parameter $a = 0.481059$ nm (JCPDS File No 4-777). It has a wide band-gap of 7 eV, making it useful for electrical isolation applications, such as cooling blankets for nuclear reactors[1]. This binary oxide is often investigated as a component in catalytic powder materials or cements[2,3]. It can also be used as a dopant to modify the electrical and optical properties of materials like ZrO_2 and HfO_2[4,5]. Band structure calculations have shown that the vacancy in CaO has an associated magnetic moment, making this material attractive as a magnetic semiconductor[6]. Based on these peculiar properties and interesting phenomenon, the intricate interplay between topological order and ferromagnetism (FM) is expected to give rise to a variety of unconventional effects that may lead to new device paradigms[7].

Previously, Kambe et al. used a two-stage process by first depositing the $Ca(OH)_2$ on MgO substrate using pulsed laser deposition (PLD). The $Ca(OH)_2$ films were then annealed to obtain the CaO films[8]. To fix the orientation irrespective of the substrate temperature and the oxygen pressure, a metal layer should be anchored tightly on the substrate. An oxide film is then formed by thermal annealing, while maintaining the orientation. At present, many metal oxides are not magnetic, but the materials can be made ferromagnetic by certain technical means, such as introducing vacancy and magnetic ion doping[9-16]. In this work, the variation of deposition conditions for CaO films was carried out using pulsed-laser deposition (PLD). We analyze their structure and experimentally studied the influence of defect on the ferromagnetism in these films.

2 Experimental

The CaO target is prepared by standard solid-state reactions. The CaO films were first deposited on the (111)-oriented yttrium-stabilized zirconia (YSZ) substrates by PLD using a 248-nm KrF excimer laser with the repetition rate of 5 Hz and an energy of 180 mJ/pulse. The target-substrate distance and laser energy were kept at 5 cm and 2 J/cm^2, respectively. During the deposition of CaO films, the substrate temperature is kept at 350 ℃ and the oxygen pressure is maintained at 0.01 mTorr and 100 mTorr, respectively. After deposition, the films are annealed at 400 ℃ in an oxygen atmosphere. Three series of films were prepared by varying one of the following parameters: as-grown, O_2 annealing, and vacuum annealing.

The films are structurally characterized by X-ray diffractions (XRD) using Cu Kα1 radiation. The doping levels and the bonding characteristics were determined by X-ray photoelectron spectroscopy (XPS, VG ESCALAB 210). The measurements of magnetic properties were carried out using the Vibrating Sample Magnetometer (VSM, Lakeshore 7304).

3 Results and discussion

Fig. 1(a) shows the X-ray $2\theta-\omega$ linear scan of the CaO film on the YSZ (111) substrate. It is found that the film is a single phase with (lll) peaks (l = 1, 2). Fig. 1(b) shows the wide-scan XPS spectrum of the CaO films. Only Ca, O and C elements present in these films, indicating that the films are pure and not polluted by any other magnetic impurities. The presence of carbon originates from the test item. The thickness of the film is ~320 nm.

Fig. 2 shows the magnetization (M) versus magnetic field (H) for the CaO bulk (i. e. , a piece

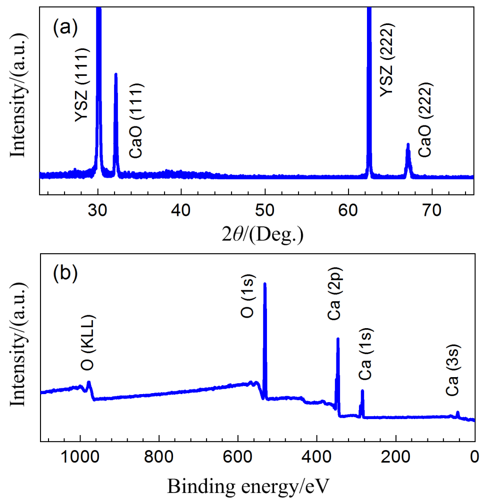

Fig. 1 (a) XRD 2θ-ω of CaO films grown on YSZ(111) substrates. and (b) XPS spectrum for CaO films with 320 nm

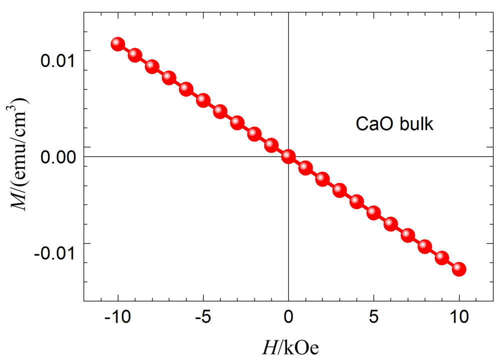

Fig. 2 M-H curve of the CaO bulk

cut from the corresponding target). It is seen that the CaO bulk is absolutely diamagnetic without any paramagnetic or ferromagnetic signals. The red line in Fig. 3 shows the M-H curve measured at 300 K of the CaO film grown at 0.01 mTorr, where a well-defined hysteresis loop is obtained, indicating that this CaO film exhibits ferromagnetic property at room temperature (RT). This M-H curve has been corrected for the diamagnetic substrate. The M-T curve recorded with $\mu_0 H = 0.5$ T in the inset of Fig. 3 demonstrates that the CaO film exhibits ferromagnetic property in the whole temperature range below 400 K, indicating that the CaO film has a high T_c above 400 K and a large saturated magnetization of ~ 25 emu/cm^3. Because both Ca^{2+} and O^{2-} are nonmagnetic, there is no source for magnetism in pristine CaO films, and YSZ(111) substrate is nonferromagnetic either[17,18]. Theoretical calculations have predicted that magnetism can be induced by defects in nonmagnetic oxides. Previous studies have shown that defect-induced magnetism exists in the CaO powders[2], while no report has been published about the magnetic CaO film so far. Here, the CaO film is experimentally proven to be ferromagnetic.

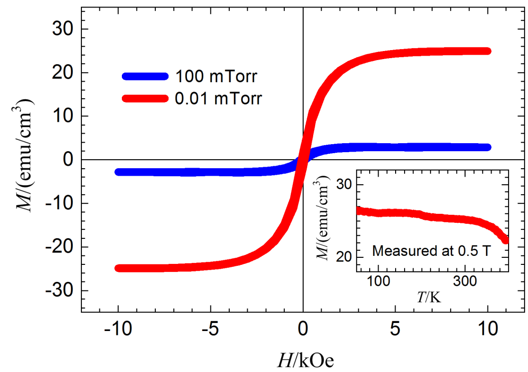

Fig. 3 M-H curves of CaO films for 100mTorr and 0.01mTorr, The inset in this figure shows the M-T curve of CaO films grown at 0.01 mTorr

The blue line in Fig. 3 shows RTM-H hysteretic loop for the CaO films deposited at 100 mTorr. Compared with the CaO films grown at 0.01 mTorr, the curve of the CaO films grown at 100 mTorr clearly show that the saturated magnetization is immensely reduced. According to the previous theoretical and experimental researches, magnetism can also be observed in nonmagnetic films such as TiO_2, HfO_2 and ZnO stem from oxygen defects or cation defects. As is known, films deposited in high vacuum have more oxygen defects than those deposited in a low vacuum. Consequently, we infer that the magnetism in CaO films originates from oxygen defects.

In order to check the effects of oxygen vacancies in stimulating the magnetism in CaO films, oxygen-annealing studies were performed. To make sure that the magnetism change is exclusively induced by oxygen-annealing, three samples were simultaneously prepared and then two of them were picked out and annealed at 400 ℃ in flowing oxygen for 0.5 h and 1 h, respectively. As shown in Fig. 4(a), after annealing in an oxygen atmosphere for 0.5 h, the saturated magnetismof the CaO film dramatically reduced from 25 emu/cm^3 to 7.4 emu/cm^3. Then, the saturated magnetism further decreases to be 3.9 emu/cm^3 with increasing the duration of annealing time up to 1h. We infer that the samples will become diamagnetic on the condition that the annealing time is long enough, which has been reported in Sr_3SnO/c-YSZ/Si heterostructures before. This evidence clearly demonstrates that oxygen vacancies contribute directly to the magnetism in those systems of undoped oxides. Reducing the concentration of oxygen vacancies could destroy the ferromagnetic interactions and impair magnetic moments.

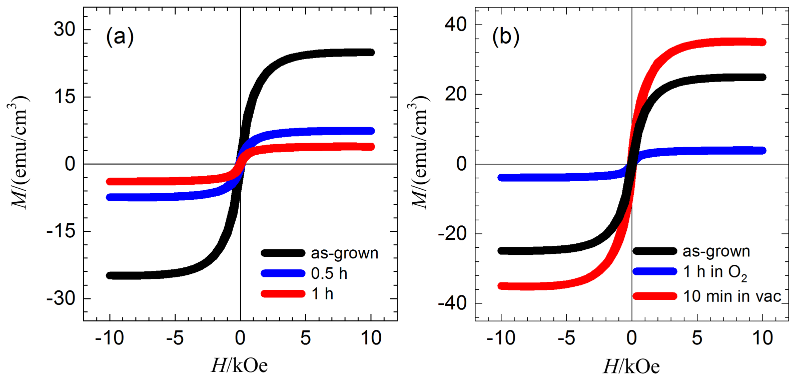

Fig. 4 (a) M-H curves of CaO films and annealed in oxygen atmosphere for 0.5h and 1h and (b) in vacuum annealed at 400 ℃ and 0.01 mTorr after O_2 annealing

Another procedure was performed to investigate the effects of oxygen vacancies on the magnetism of the CaO films. A sample was first annealed in an oxygen atmosphere for 1 hour and then annealed in vacuum (~ 0.01 mTorr) for 10 min, as shown in Fig. 4(b). It is found that the saturated magnetism of the CaO film annealed in vacuum (~ 0.01 mTorr) for 10 min was statistically higher than those annealed in an oxygen atmosphere for 1 hour. Also, the saturation magnetization of the films annealed in vacuum (~ 0.01 mTorr) for 10 min is larger than the as-grown films. Therefore, it can be concluded that oxygen vacancy is related to the magnetism of the CaO films.

4 Conclusion

In conclusion, we have investigated the magnetic properties of CaO films prepared by PLD. The *M-T* and *M-H* curves of the CaO films show that these films are ferromagnetic in the temperature range below 400 K. The experimental results have demonstrated that the oxygen vacancy is the reason for the magnetic order in CaO films.

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