Origin of ultraviolet photovoltaic effect in Fe$_3$O$_4$ thin films

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We have investigated the transport and ultraviolet photovoltaic properties of Fe$_3$O$_4$ thin films grown on glass substrates by facing-target sputtering technique. The nonlinear dependence of current-density on voltage suggests that the transport process is most likely the tunnelling process and grain boundaries act as barriers. Furthermore, non-equilibrium electron-hole pairs are excited in the grains and grain boundary regions for Fe$_3$O$_4$ film under ultraviolet laser, since the energy gap of Fe$_3$O$_4$ is smaller than the ultraviolet photon energy. And then the built-in electric field near the grain boundaries will separate carriers, leading to the appearance of an instant photovoltage.

**Keywords:** photovoltaic effect, magnetite, thin film

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The half-metallic nature of magnetic electrodes for tunnelling junction devices is expected to induce a large magnetoresistance (MR), and half-metallic materials have been considered as important potential materials for future spintronics which takes full advantage of electrons’ spins as well as their charge in information circuits.$^{[1-3]}$ Theoretical band structure calculation shows that there is a gap in the majority spin band at the Fermi level but no gap in the minority spin band for magnetite (Fe$_3$O$_4$), predicting that Fe$_3$O$_4$ is half-metallic and provides 100% spin-polarized conduction electrons.$^{[4,5]}$ In magnetite films the presence of antiphase boundaries (APB) has been revealed as natural growth defects, and the magnetic coupling at the boundaries is antiferromagnetic (AF$^6$)$^{[6,7]}$. Due to the high degree of spin polarization in magnetite, the presence of these AF boundaries enhances the resistance of the films and the grain boundaries (GBs) act as a more high resistive tunnel barrier. In this paper, we report the optical response of Fe$_3$O$_4$ film under a pulsed ultraviolet (UV) laser irradiation, and this photovoltaic effect can be understood by considering the built-in electric field near the GB separating nonequilibrium electron-hole pairs.

To prepare magnetite films, Fe (100nm) thin films were fabricated on glass substrates by the facing-target sputtering technique at room temperature (RT).$^{[8,9]}$ The corresponding sputtering rate is 0.092nm/s. And then the Fe films were oxidized for 1800s at about 350°C in an oxygen atmosphere of 8 Pa by plasma of 40W. Following oxidation, the films were cooled to RT in a vacuum of about $2\times10^{-3}$ Pa. The structures of the Fe$_3$O$_4$ films have been characterized by x-ray diffraction (XRD) using Cu K$\alpha$ radiation, and the $\theta-2\theta$ scanning profile exhibits only one peak corresponding to the (531) orientation of the Fe$_3$O$_4$ phase. The surface morphology was further examined by atomic force microscopy (AFM) as shown in Fig.1. The root-mean-square surface roughness is $\sim$ 6.8 nm averaged over an area of $1\mu$m x $1\mu$m. The av-

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verage grain size, \( D \sim 80 \text{ nm} \), has been determined by the linear intercept method: i.e., from the number of the line crossings.

![AFM image of the Fe\(_2\)O\(_4\) thin film grown on a glass substrate (image size: 1\( \mu \text{m} \times 1\mu \text{m} \).](image)

Figure 1. AFM image of the Fe\(_2\)O\(_4\) thin film grown on a glass substrate (image size: 1\( \mu \text{m} \times 1\mu \text{m} \)).

Figure 2 shows the current density–voltage \((J-V)\) characteristic of Fe\(_2\)O\(_4\) film taken in current-in-plane geometry with a standard linear four-probe dc method at RT. The curve is highly reproducible and does not show any significant hysteretic behaviour when the bias is cycled. Hence, the whole curve is antisymmetric against the origin. For lower bias, an ohmic conduction is observed. When the bias \( V \) attains a threshold value \( (V_{th} \sim 0.167 \text{V}) \) and corresponding current density approaches \( J_{th} \sim 75 \text{Acm}^{-2} \), nonlinear conduction sets in, suggesting that the transport process for the Fe\(_2\)O\(_4\) film is most likely the tunnelling process and a kind of energy barrier/gap exists between adjacent grains. When the applied voltage \( V \) exceeds \( V_{th} \), the energy barrier is overcome and the avalanche-like effect appears. A roughly fit of our \( J-V \) characteristics to the Simmons model predicts reasonable parameters for the mean barrier height and width, \( \Phi_0=0.18\text{eV} \) and \( b=1.84\text{nm} \), which is consistent with the width of the GBs of Fe\(_2\)O\(_4\) (100 nm) film, \( \sim 2\text{nm} \), reported by Eerenstein et al using the effective medium approximation\,[7]

![Figure 2. \( J-V \) characteristic of Fe\(_2\)O\(_4\) thin film at RT. \( J_{th} \) and \( V_{th} \) denote the threshold values. The solid line is a guide for the eye.](image)

Figure 3 presents a typical photovoltage transient of Fe\(_2\)O\(_4\) film on a glass substrate under a pulsed laser irradiation of 308 nm and 25 ns in duration \((\tau)\). The energy density is 0.5 mJ/mm\(^2\) and the irradiated area is 5mm\( \times \)5mm. The pulse response was monitored with a 500-MHz sampling oscilloscope terminated with a resistance of 50 \( \Omega \). The photovoltaic response shows a full width at half maximum of 30ns, suggestive of the lifetime of 30 ns for the nonequilibrium photo-induced carriers. A simplified model can be given on the origin of the photovoltaic signal. Since the Fe\(_2\)O\(_4\) film consists of grains separated by GBs (e.g. APBs), there is a chemical potential shift \( \Delta \mu \) between the GB region and the grain. This might induce a depletion layer in the GB region, and the build-in voltage \( V_b \) is given by \( \Delta \mu \), \( V_b = \Delta \mu \). When the laser irradiates the sample, electron-hole pairs can be excited in the grains and the GB regions since an energy gap of 0.14 eV (the theoretic value is 0.19eV)\,[11,12] for Fe\(_2\)O\(_4\) between occupied and empty electronic states is much smaller than ultraviolet (UV) photon energy (4.0 eV for 308 nm). And then the nonequilibrium carriers are separated by the built-in electric field near the GB, eventually leading to the appearance of an instant photovoltage. Especially, the signals depend linearly on the distance between \( A \) and \( B \).
Fig. 3. Photovoltaic signal of an Fe$_3$O$_4$ film irradiated by a 308 nm laser pulse of 25 ns duration. The inset shows a schematic circuit of the sample measurement; here, $A$ and $B$ denote the electrodes.

Since the sample is polycrystalline, there should be an equal number of grains with photogenerated carriers shifting in one direction as in the opposite direction, hence there should not be net current flow and no photovoltage signal. This is not the case. In fact, it is uncertain why there is an overall preferred direction for the flow of the photogenerated current. This behaviour may be due to the asymmetry of the lattice which induces an asymmetric movement of the excited carriers in a preferred direction. Further study on the nature of the photovoltaic properties of such a system is under way.

In summary, we have observed non-ohmic $J$–$V$ characteristics in magnetite films, suggesting that the transport process is most likely the tunnelling process and the GBs act as barriers. In particular, since UV photon energy is much higher than the energy gap of Fe$_3$O$_4$, the electron-hole pairs are excited in the film under UV laser, and separated by the built-in electric field near the GBs, leading to the photovoltaic effect.

References