Photoemission electronic states of epitaxially grown magnetite films

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Abstract

The valence band photoemission spectra of epitaxially grown 300 Å single crystalline magnetite films were measured by the angle-resolved ultraviolet photoemission spectroscopy (ARUPS) at 300 K. The samples were grown either on MgO(0 0 1) (B termination) or on (0 0 1) Fe (iron-rich A termination), thus intentionally presenting different surface stoichiometry, i.e. also different surface electronic states. Four main features of the electron photoemission at about −1.0, −3.0, −5.5 and −10.0 eV below a chemical potential show systematic differences for two terminations; this difference depends on the electron outgoing angle. Our studies confirm sensitivity of angle resolved PES technique on subtleties of surface states.
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1. Introduction

Magnetite is an inverse spinel with Fe^{3+} residing on tetrahedral (A) positions of the oxygen lattice and with both Fe^{3+} and Fe^{2+} existing on the octahedral (B) sites. One electron from each two B sites may be considered traveling freely on all those positions making magnetite relatively good conductor among oxides. Since, additionally, in this strong ferrimagnet (Neel temperature is ca. 850 K) all octahedral ions have magnetic moments antiparallel to tetrahedral ones, the electrical transport should be spin polarized. And even though some recent measurements question the orthodox meaning of ions [1] and even the low temperature inverse spinel character of magnetite [2] suggesting band electrons rather than ionic model, in each electron band structure calculations half metallic state at ambient temperature is yielded [3,4]. This spin polarized transport makes magnetite very promising material for spintronic applications, even in view of the fact that 100% polarization was never found experimentally [5,6]. Thus, the understanding of the electronic states and the way to tailor them becomes very essential.

However, the nature of electronic states in magnetite is by no means clear. Although in their photoemission studies Chainani et al. [7] claim magnetite being metallic at ambient temperature, band splitting even above the Verwey temperature $T_V = 120$ K was observed again in photoemission experiments by Park [8]. The same conclusion was also inferred from the recent photoemission studies [9]. Also the nature of the interactions involved are not definitely established. The electron–electron interactions as being of primary importance were postulated, starting from the seminal work of Anderson [10], but the carriers in magnetite are also strongly confined to the lattice which means that magnetite is a small polaron material [9]. In any case, the problem of the nature of electronic states in magnetite is still open, and the experimental means for electronic states characterization should be optimized. Additionally, since in spintronic application mainly thin film structures are used, the goal is to understand the nature of surface electronic states and how those states are reconstructed in comparison to the bulk materials.

Ultraviolet photoemission electron spectroscopy and its variations as spin polarized PES and angle resolved PES (e.g. angle-resolved ultraviolet photoemission spectroscopy ARUPS) are very frequently used tools to study the valence band in materials. Surface states of magnetite (1 0 0) on MgO were recently studied by spin polarized PES [6]. It was also shown [9] that

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only surface related electronic states can be revealed by the low energy (ca. 20 eV) photoemission and those surface states are largely distorted in comparison with bulk states that were observed by the higher energy (ca. 700 eV) incident radiation. In view of those results the aim of the present studies it to use low ultraviolet radiation in order to measure low energy angle resolved PES for two different terminations of MBE-grown magnetite single crystalline film and to see to what extend the subtleties of surface electronic states may be studied by this technique. Here only a few preliminary results are presented.

2. Surface structure and sample preparation

Epitaxial magnetite films can be easily grown by reactive deposition of Fe on MgO(0 0 1) [11]. Such films expose the (0 0 1) surface that can nominally be terminated by a layer consisting of Fe ions in tetrahedral positions (so called A-layer) or by a mixed oxygen-octahedral Fe layer (B-layer). Both bulk-like terminations are polar and a number of models assume that the charge neutrality condition is a driving force behind the $(\sqrt{2} \times \sqrt{2})R45°$ reconstruction typical for the $Fe_3O_4(0\,0\,1)$ surface. The obvious way to explain the autocompensated $Fe_3O_4(0\,0\,1)$ surface with the observed reconstruction is to remove certain surface atoms: half of Fe^{3+} ions for the A termination [12] or a number of oxygens for the B termination [13]. However, surface stability can be achieved also through electronic degrees of freedom [14]. Thus, models with full B-type layer termination with a specific surface electronic and geometric structure, as a surface charge ordering [15,16] or the Jahn–Teller distortion [17], were also proposed. The existence of the A termination [18] is problematic, mainly due to ambiguity of the surface stoichiometry, since there were no procedures to control whether the surface layer was oxygen or iron rich. Recently, we proposed a new method of preparing the $Fe_3O_4(0\,0\,1)$ surface by oxidizing Fe(0 0 1) films or by depositing magnetite on Fe(0 0 1) films, which results in high-quality and impurity-free surfaces with $(\sqrt{2} \times \sqrt{2})R45°$ reconstruction and reproducible atomically resolved STM images [19]. This, in turn, allowed us to give a model of the surface structure for this type of preparation. The surface is terminated with a half-filled A-layer containing tetrahedral Fe^{3+} cations, fulfilling the neutrality condition. Pairs of Fe^{3+} cations approach along the $\langle 1\,1\,0 \rangle$ direction forming dimers. In different surface areas, the dimers are arranged either in a 8.4 Å × 8.4 Å or in a 12 Å × 12 Å square lattice. The reconstruction is driven by the charge-ordered subsurfaces B-layer. Such a termination can be easily distinguished from the oxygen rich B-one by the character of the STM atomic images and also be the Auger spectra displaying different iron to oxygen signal ratio. While the films obtained directly on MgO during classical preparation give the Auger signal ratio of the 510 eV oxygen to 651 eV iron lines equal to R = 3.34(5), very close to that reported by Ruby et al. [20], the respective R value for magnetite films on Fe is reduced down to 2.96(5), indicating an iron rich termination.

For the present studies a thin film sample was prepared combining both terminations. For this purpose a cleaved 10 mm × 10 mm MgO(0 0 1) substrate was used. After introduc-

ing into the UHV system (base pressure below 1×10^{-8} Pa) and a standard degassing at 500 °C, a 200 Å buffer layer of epitaxial Fe(0 0 1) was deposited on a half of the MgO plate. On the substrate prepared in this way, held at 250 °C, a 300 Å $Fe_3O_4(0\,0\,1)$ film was grown by oxygen-assisted deposition of Fe at the O_2 partial pressure of 10^{-4} Pa. Finally, the sample was annealed at 500 °C for 60 min. The as-prepared films were characterized *in situ* by Auger electron spectroscopy confirming different surface stoichiometry of both parts of the sample. For the ARUPS measurements the sample was transferred to a separate UHV system using a transportable vacuum chamber at the pressure below 1×10^{-6} Pa.

3. ARUPS results and their analysis

ARUPS spectra were collected at 300 K with the Photoelectron Spectrometer equipped with the high energy resolution (70 meV, calibrated for the Fermi edge of Ag) analyzer AR 65 of photoelectron kinetic energy (Omicron). The high intensity ultraviolet radiation (energy $h\nu = 21.2$ eV) from the helium source (from FOCUS) hit the sample surface at the variable angle θ and out-coming electrons were recorded under the angle ϕ, both angles measured with respect to the (0 0 1) surface normal. Binding energies (BE) are related to the Fermi level and the background was subtracted according to standard procedure.

Selected spectra for the UV incidence angle $\theta = 20°$ and different out-coming electron angles ϕ are shown in Fig. 1. Four main features of the electron photoemission at about −1.0, −3.0, −5.5 and −10.0 eV show systematic differences for both terminations of the magnetite film. Those results are compared for a few ϕ angles in Fig. 2 and it is clear that the dispersion relations are different. The low BE parts of the spectra up to −2 eV for $\phi = 20°$ through −3 eV for $\phi = 50°$ and to −4.2 eV for $\phi = 60°$ are exactly the same for all angles. On the contrary, higher energy parts (−4 to −12 eV) significantly differ. In the inset of Fig. 2 two spectra for BE = −10 and −5.5 eV are plotted versus ϕ angle. Since curves for Fe_3O_4/MgO cross the relevant
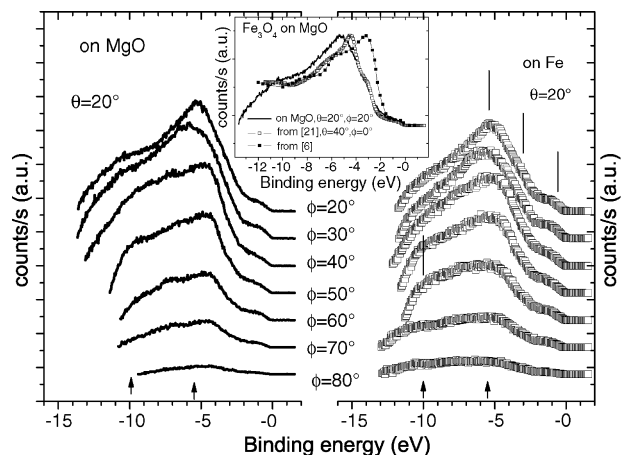

Fig. 1. Selected ARUPS valence band spectra of both magnetite thin film terminations for indicated angles. The vertical lines point to four main features of the spectra. The arrows mark the energies where comparison between curves is made in the inset of Fig. 2.
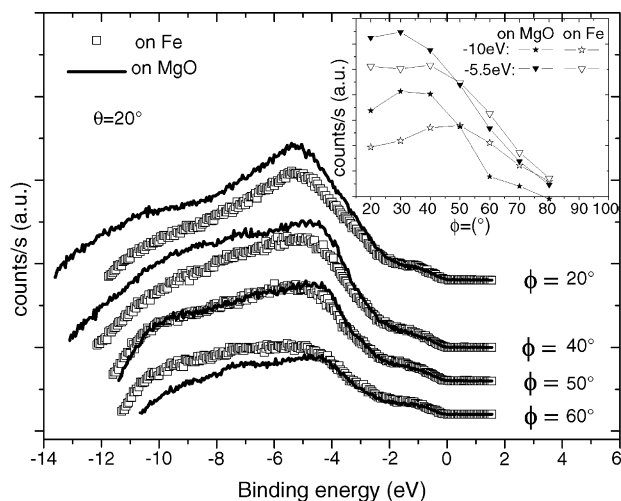
Fig. 2. Comparison of ARUPS spectra for Fe_3O_4 film grown on MgO and Fe. In the inset the out-coming photoelectron ϕ dependence is plotted for two energies -10 and -5.5 eV.

data for Fe_3O_4/Fe, the difference between the spectra from both terminations is caused mainly by the more pronounced ϕ-variation of Fe_3O_4/MgO. In other words, it is the intensity of Fe_3O_4/MgO that goes over the intensity of Fe_3O_4/Fe for $\phi < 50°$.

The lower BE part with the pronounced emissions at -1.0, -3.0 and -5.5 eV [21] is dominated by the Fe 3d states, as is clear from band structure calculations [3,4,6]. The termination-sensitive part from -7 to -12 eV is mainly due to 2p oxygen states with some contribution from Fe 3d states [3,4,6]. It means that for those higher energies, the occupation of mixed oxygen-iron states are larger for Fe_3O_4/MgO than for Fe_3O_4/Fe for photoelectrons out-coming in the direction perpendicular to the surface, but this proportion is reversed for electrons leaving the surface under smaller angles.

In the inset of Fig. 1 photoemission results from three different magnetite samples grown on MgO are compared. Although for each sample different point in the Brillouin zone was probed (actually, the data from [6] was collected on spin polarized PES which results in data averaging over several k-vectors), the difference between curves is too large to be caused by this fact and, most probably, reflects distinct electronic structure of our sample, in comparison to, e.g. that from [6].

In conclusion, we have presented preliminary results from ARUPS studies performed on two different terminations of the same MBE-grown 300 Å single crystalline magnetite. The

results suggest that the electronic surface states for MgO grown sample have more pronounced dispersion than those for other termination.

Acknowledgement

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