

Location of Trapped Electron Centers in the Bulk of Epitaxial MgO(001) Films Grown on Mo(001) Using *in situ* W-band Electron Paramagnetic Resonance Spectroscopy

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We present the first *in situ* W-band (94-GHz) electron paramagnetic resonance (EPR) study of a trapped electron center in thin MgO(001) films. The improved resolution of the high-field EPR experiments proves that the signal originates from a well-defined species present in the bulk of the films, whose projection of the principal g -tensor components onto the (001) plane are oriented along the [110] direction of the MgO lattice. Based on a comparison between the structural properties of the films, knowledge of the ability of bulk defects to trap electrons, and the properties of the EPR signal, it is possible to propose that the paramagnetic species are located at the origin of a screw dislocation in the bulk of the film.

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Metal oxides play an important role for a wide variety of technological applications. A great deal of effort has been made in the past to elucidate the intricate relationship between the structure and the properties of these materials. The complexity of the problem is increased significantly by the presence of defects, which determine many of the chemical, optical, and electronic properties of oxide materials. Topological defects play an important role in this respect. This is well documented for surfaces where steps, kinks, or vacancies were found to modify various surface properties such as molecular adsorption, charge trapping, luminescence, or catalytic activity [1–7]. Another class of topological defects are dislocations, which are key for a variety of important processes such as corrosion (e.g., in biomedical implants) or the insulating properties in oxide dielectrics within a transistor or memories. The structural and mechanical properties of dislocations have been studied for some time, but their electronic and chemical properties remain less well understood [8]. These species are mainly located in the bulk, but they often terminate at the surface and, hence, can interact with surface processes [9]. An important property of some structural defects is their ability to trap charges. Even for bulk species, charge-transfer processes to the surface have been shown to occur, and they can play an important role for the chemistry at oxide surfaces; this has been demonstrated using bulk doping of oxide films [10–12].

One of the oxides most frequently studied in this respect is MgO, a material important for applications in electronics and catalysis [13]. MgO is a useful model system because of its high ionicity and simple rock-salt structure. Bulk defects as well as their counterpart on the surface have been investigated extensively. Electron paramagnetic resonance (EPR) spectroscopy has provided valuable information for characterizing paramagnetic defects such as trapped

electrons [4,5,14–16]. A particular strength of EPR spectroscopy is its ability to probe the environment of the species encoded in the characteristic magnetic parameters, such as the g tensor in the case of the Zeeman interaction. The anisotropy of the Zeeman interaction, governed by spin-orbit coupling, reflects the local symmetry of the spin centers. In turn, the principal components of the g tensor coincide with high-symmetry directions of the local environment. The investigation of a single crystalline material with a well-defined relationship between the crystal lattice and the laboratory framework allows us to determine not only the principal components, but also the orientation of the g tensor with respect to the crystal lattice. However, the g -tensor anisotropy of trapped electron centers in the bulk or on the surface of MgO is often very small. Therefore, the spectral resolution of commonly used X-band (9-GHz) EPR spectroscopy is insufficient to resolve the anisotropy; this hampers a detailed analysis of the local environment of the species under consideration. For paramagnetic centers whose magnetic resonance spectrum is governed by the Zeeman interaction, increasing microwave frequency will increase spectral resolution. Herein we will demonstrate for the first time that *in situ* W-band (94-GHz) EPR spectroscopy increases the spectral resolution of paramagnetic radical centers in MgO(001) films. The additional information extracted from these measurements allows us to deduce the location of trapped unpaired electrons present in domain boundaries of epitaxial, single-crystalline MgO(001) films grown on Mo(001).

Magnesium oxide thin films were prepared by reactive deposition of Mg in an oxygen atmosphere (10^{-6} mbar) at a growth rate of 1 ML min^{-1} . The films were grown on a Mo(001) substrate, cleaned by repeated sputter (300 K) and anneal (flashes to 2200 K) cycles. X-band EPR experiments using a TE₁₀₂ resonator were carried out in an UHV

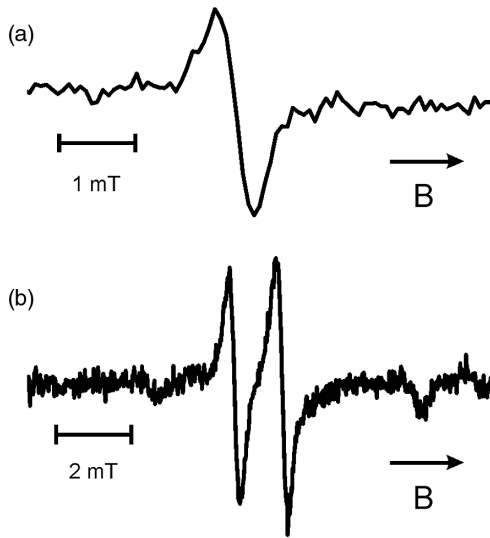


FIG. 1. EPR spectra of pristine MgO(001) films grown on Mo(001) at 300 K: (a) X-band EPR spectrum ($T = 30$ K) of a 20-ML-thick film ($\phi = 0^\circ$); (b) W-band EPR spectrum ($T = 50$ K) of a 30-ML-thick film ($\phi = 12^\circ$). The magnetic field is oriented in the surface plane. ϕ denotes the angle between the magnetic field and a [110]-equivalent direction of the MgO lattice.

chamber equipped with standard facilities for thin-film preparation and characterization, which has been described in detail elsewhere [17]. W-band EPR experiments using a home-built Fabry-Perot resonator were performed in an UHV apparatus comprising a preparation chamber as well as a dedicated chamber for the EPR measurements, as described in detail elsewhere [18]. Microwave power and modulation amplitude were chosen to avoid saturation or overmodulation effects. Simulations of the EPR spectra were performed using the easyspin package [19].

Figure 1(a) shows the X-band (9-GHz) EPR spectrum of a pristine 20-ML-thick MgO(001) film grown on Mo(001) at room temperature with the magnetic field oriented in the surface plane along the [110] direction. The spectrum exhibits a single resonance close to the g value of the free electron with a linewidth of 0.55 mT. The resonance position close to the g value of the free electron is typical for trapped electrons in defect sites of MgO [4,9,15,20–27]. The presence of paramagnetic species in pristine films is in contrast to previously reported MgO films grown at 600 K, which show no indication for the presence of paramagnetic electron centers [4]. These centers do not react with molecules from the gas phase (such as N_2O , CO, or H_2), nor is it possible to alter their relaxation properties by the adsorption of thick layers of molecular oxygen at low temperature. From this behavior it is concluded that the signals are not associated with surface species, but rather paramagnetic centers located in the bulk of the film. The signal is observed for films thicker than 10 ML and obeys constant intensity for films thicker than 20 ML. Based on calibration with EPR signals of Au atoms, the signal

intensity of the 20-ML film corresponds to $5 \pm 2 \times 10^{12}$ spins. This corresponds to an average distance of several nm, which renders spin-spin interaction between the species unlikely. The signal disappears upon annealing of the film to 800 K. The intensity decreases in a sigmoidal fashion with a turning point at about 550 K (data not shown). The thermal stability is comparable to the one found for electrons trapped in misfit dislocations of annealed MgO(001) film using H atoms as electron source; however, the signal is more narrow and shifted to lower fields ($\Delta g = 0.0002$) [9].

Angular-dependent measurements, changing the angle of the magnetic field with respect to the surface normal, show very little change of the resonance position and a slight reduction of the linewidth. This result further corroborates the assignment of the observed species to trapped electron centers, as it shows that all three g -tensor components have to be quite similar. This excludes the presence of oxygen-based paramagnetic centers, which would have at least one g -tensor component shifted significantly to higher g values [22,27–31]. Rotation of the magnetic field in the surface plane, as exemplified by a measurement with the magnetic field oriented along the [100] direction of the MgO lattice, results in the same resonance position. In case of a paramagnetic color center (F^+ center) in the bulk of MgO, an isotropic g value would be expected [14]. These centers are high-energy species as compared to electrons trapped at morphological defects, such as domain boundaries or screw dislocations [32,33]. The latter, however, exhibit an anisotropic environment; in turn, they will exhibit an anisotropic g tensor, whose principal components will be oriented along the high-symmetry directions of the site trapping the electron.

To improve the spectral resolution the same system was studied using *in situ* W-band (94-GHz) EPR spectroscopy [18]. In contrast to the single line observed at X-band frequency, the W-band spectrum [Fig. 1] shows two lines split by 1.32 mT with approximately the same intensity. The positions were determined to be $g = 2.00272$ and $g = 2.0036$ using 2,2-diphenyl-1-picrylhydrazyl (DPPH) as an external standard. The accuracy of the absolute g value is limited to that of the DPPH standard (2.0036). The linewidth of both lines is 0.32 mT, which is slightly smaller than the width observed at X-band frequency. The similar intensity of the two signals suggests that they originate from the same species at symmetry-equivalent sites. However, proof for such an interpretation requires angle-dependent measurements. Figure 2(a) shows a series of angle-dependent W-band EPR spectra. The magnetic field is rotated in the surface plane and ϕ defines the angle between the magnetic field and the [110] direction of the MgO lattice. Within this series the splitting between the lines is maximal for $\phi = 0^\circ$ and vanishes at $\phi = 45^\circ$ corresponding to the magnetic field aligned with the [100] direction of the MgO lattice. The increase of the

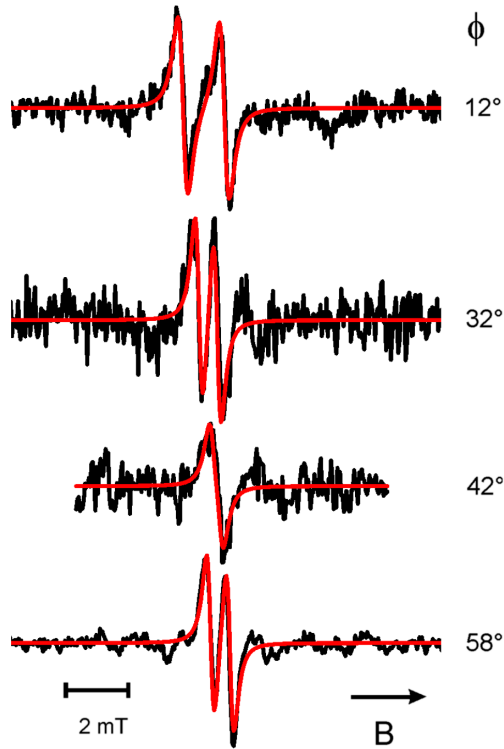


FIG. 2. Angular-dependent W -band spectra of a 30-ML-thick MgO(001)/Mo(001) film taken as a function of the in-plane angle ϕ ; the magnetic field is oriented in the surface plane and ϕ denotes the angle between the [110] direction and the magnetic field in the (001) plane.

spectral splitting at azimuthal angles above 45° provides further evidence for the fourfold symmetry of the pattern. The set of spectra can be described by g values along the two orthogonal [110]-equivalent directions of the (001) plane of $g = 2.00363$ and $g = 2.0027$, respectively. This orientation of the g -tensor components with respect to the MgO lattice already excludes trapped electron centers, such as F centers, found in the bulk of MgO [14]. At X -band frequency the observed splitting at W band would reduce to 0.15 mT, which is considerably smaller than the linewidth. This implies a single unresolved line with slightly larger linewidth at X -band frequency, which is consistent with observation [Fig. 1(a)].

Within the W -band setup it is not possible to rotate the magnetic field out of the surface plane. Therefore, it is not possible to determine the orientation of the g -tensor with respect to the MgO lattice; however, the X -band results mentioned above limit the out-of-plane anisotropy to a level comparable to the one observed in the (001) plane. Important conclusions concerning the location of the trapped electron can be drawn from the observed in-plane anisotropy of the g tensor. First, the presence of two angular-dependent lines clearly shows that the signal corresponds to one well-defined site associated with the properties of the crystalline MgO(001) film. Second, MgO

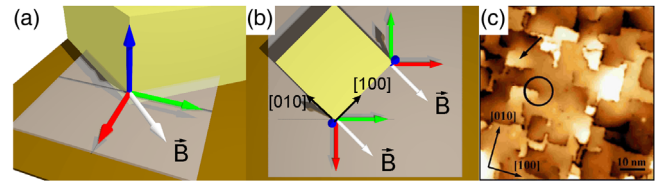


FIG. 3. Schematic representation of an edge terminating two domain boundaries within a MgO film running in orthogonal [100]-equivalent directions. For the sake of clarity the adjacent MgO necessary to form a continuous film is not shown [see the circled region in (c) for comparison]. (a) Perspective view: the white arrow represents the direction of the magnetic field oriented along the [100] direction; the red, green, and blue arrows represent the orientation of the principal components of the g tensor (for the choice of the orientation see the text). (b) Top view of the scenario in (a); a second symmetry-related edge together with the corresponding g tensor is drawn in. (c) STM image of a 15-ML-thick MgO(001) film grown at 300 K and subsequently annealed at 1070 K ($U = 4.8$ V) (reproduced with permission from [34]). The black circle indicates a region schematically shown in (a) and (b).

exhibits a simple rock-salt structure and, hence, a fourfold symmetry in the (001) plane. This fourfold symmetry of the crystal is lifted by an external magnetic field, which results in four symmetry-related lines in case of an arbitrarily oriented g tensor. The presence of only two lines, which collapse for the magnetic field along an [100]-equivalent direction, allows us to further restrict the orientation of the g tensor. Two of the principal components of the g tensor have to be symmetrically oriented with respect to a plane spanned by the surface normal and a [100] direction, which is indicated by the white arrow in Fig. 3(a). As shown in Fig. 3(b), the fourfold symmetry of the surface requires the presence of four symmetry-equivalent sites. For a magnetic field oriented along the [100] direction, all four sites have the same resonance position [Fig. 3(b)]. In contrast, all other orientations will give rise to two resonances, which is easily seen for a magnetic field along [110]. For two of the sites, the magnetic field vector would be aligned with the red component of the g tensor; for the other two sites, it would be aligned with the green one [Fig. 3(b)].

The important question of where such sites might be located remains to be determined. The orientation of the g -tensor projections in the (001) plane already excludes species known from bulk MgO, such as F_c centers [14]. Structural investigations of MgO(001) films on Mo(001) have shown that the lattice mismatch between MgO(001) and Mo(001) of -5.2% for an epitaxy relation MgO[110]||Mo[100] is relaxed for thicker films [34]. The relaxation of the lattice mismatch can be greatly improved for films below approximately 15 ML by annealing the films to about 1000 K. Above approximately 15 ML, annealing the films does not increase the in-plane lattice constant as compared to the room-temperature

preparation; however, it does improve the long-range order of the film as well as the smoothness of the surface. Figure 3(c) shows a STM image [34] of a 15-ML-thick film clearly revealing the presence of screw dislocations, which results in islands of 10–30 nm width, separated by domain boundaries running in [100]-equivalent directions. Diffraction experiments show that the annealed films release a large fraction of the strain within the first 7 ML by the formation of a periodic network of misfit dislocations running along the [110] direction of the MgO lattice [34]. With respect to these results, it is important to note that the EPR signal is found only for films thicker than 10 ML. The number of paramagnetic centers increases rapidly above 10 ML, but saturates below 20 ML to stay constant for thicker films (data not shown). This indicates that the paramagnetic centers are formed in a thickness range where the strain in the lattice is already significantly reduced for films grown at room temperature [34].

Defects within misfit dislocations running in the [110] direction of the MgO lattice would be possible candidates to accommodate unpaired electrons characterized by an orientation of the g tensor, consistent with the experimental observations. However, misfit dislocations were found to be most effective to reduce large strain at small film thicknesses. For thicker films, where most of the strain is already released [34], screw dislocations with corresponding domain boundaries running in a [100] equivalent direction were found, as shown in Fig. 3(c) [34]. The paramagnetic sites characterized by EPR spectroscopy in this study are found in a region between 10 and 20 layers from the Mo(001) support, in which strain is already largely released [35]. For these films, screw dislocations are suitable sites consistent with the observed EPR signal. The observed local symmetry of the site exists at the two terminating ends of these defects. The ones observed here are located in the bulk, most probably in the region where the strain-release mechanism changes between the two modes discussed above. The ability of screw dislocations to trap electrons, and that of domain boundaries with a local arrangement of atoms with the same local symmetry, was already shown theoretically, which gives further credit to this interpretation [33,36].

In conclusion, we have shown that *in situ* W-band EPR spectroscopy provides experimental evidence for a well-defined paramagnetic species present in the bulk of epitaxially grown MgO(001) films. Because of the observed g -tensor anisotropy and the orientation of the g -tensor components in the (001) plane along the [110] direction, bulk color centers of MgO can be excluded [14]. From a combination of structural studies of MgO(001)/Mo(001) films and the evolution of the EPR intensity as a function of film thickness, it is possible to assign the EPR signals to electrons trapped at the core of screw dislocations of the MgO film.

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