Energies and Dynamics of Photoinduced Electron and Hole Processes on MgO Powders

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The dynamics of photoinduced formation of electron and hole centers at the surface of MgO powder has been investigated in situ using EPR spectroscopy. Monochromatic excitation of the sample with 282 nm photons leads to creation of well-separated electron and hole centers at the surface. Polychromatic (200−900 nm) irradiation leads to a very different time evolution of the EPR signal of the photoinduced centers. We argue that this difference is due to secondary reactions stimulated by the low energy part of the radiation spectrum. It can be explained by the excitation of the localized holes to the valence band and localized electrons into the conduction band and their consequent trapping at defect states and powder particle interfaces. The results demonstrate the existence of various types of EPR active and inactive electron and hole traps at the surface of MgO powder and provide preliminary data on their energy distribution.

Introduction

Surface defects in insulating materials, such as MgO, have attracted much attention during the past years due to their role as active sites for adsorption processes and chemical reactions (see, for example, refs 1−3). Recent developments in sample preparation techniques[4−6] facilitated the production of high surface area, nanometer-sized MgO powders exhibiting high concentrations of surface defects. Sample characterization by spectroscopic methods such as UV diffuse reflectance (UV-DR),[7,8] Fourier transform infrared spectroscopy (FTIR),[9] electron paramagnetic resonance (EPR),[10,11] metastable impact electron spectroscopy (MIES),[12,13] and others provided important insights into the surface structures, spectroscopy and chemical properties of nanometer-sized MgO particles. In particular, it is now well established that some of the spectroscopic and chemical properties of the MgO surface are determined by low coordinated (LC) oxygen ions at edges, kinks and corners (see, for example refs 14 and 15). Recent scanning probe studies [16−18] supported these models by revealing the complex step and defect structure of the MgO and other insulating surfaces.

The experimental analysis of optical absorption and photoluminescence spectra of MgO powders[8,14] and recent theoretical results[19] suggested a clear correlation between the excitation energies and the coordination number of oxygen ions: the excitation energy ranges from 7.8 eV in the bulk (6-coordinated O^{2-}) to 4.6 eV at 3-coordinated anion sites. The optical absorption with maxima at around 5.4 and 4.6 eV has been attributed to 4- and 3-coordinated surface oxygen sites, respectively. However, the luminescence induced by the selective excitation of 4- and 3-coordinated anions could not be attributed unambiguously to well-defined emitting sites.[20,21] It has been suggested that excited states (excitons) created at 4-coordinated anion sites can migrate and become trapped at 3-coordinated

corner or kink sites. The possible mobility of surface excitons was also corroborated by theoretical calculations.[19]

A recent experimental study carried out in our laboratory[11] has shown, that after selective excitation of both 3- and 4-coordinated oxygen ions, and their subsequent UV-ionization, exclusively 3-coordinated hole centers (O_{3C}^{2-} ions) are detected by EPR spectroscopy. In that work, the formation of LC O^- ions in photoexcited samples was aided by oxygen molecules, which acted as electron traps. If, on the other hand, the O^- hole centers at the MgO surface are photogenerated under vacuum conditions, the released electrons are trapped at the surface of the oxide,[22,23] giving a characteristic EPR signal around the free spin value ($g_e = 2.0023$). The surface oxygen vacancies have long been considered as the most abundant surface electron trapping sites.[24] However, the discussion on the nature of surface electron traps has recently been extended to other structural defects, such as divacancies and low-coordinated surface Mg sites.[25−27] Recent calculations [26,27] provided the ionization energies and electron affinities of various surface defects on MgO nanoclusters suggesting a distribution of possible electron traps of various structures and depths.

In this paper, we investigate the dynamics of the hole and electron center EPR signals induced by mono- and polychromatic irradiation of MgO powders and provide the first clear experimental evidence for the existence of a large concentration of different electron and hole trapping sites at MgO surfaces. Our spectroscopic data provide ionization energies for some of these sites and allow us to propose a simple model of photoinduced surface reactions in MgO powder samples.

Experimental Section

All experiments were carried out on MgO nanoparticles produced by chemical vapor deposition (CVD) in a flow reactor system as described elsewhere.[28] The sample was annealed at 1173 K before each experiment to guarantee a totally dehydroxylated surface. A 300 W Xe lamp (Oriel) was used for UV irradiation. For selective excitation experiments, the light beam

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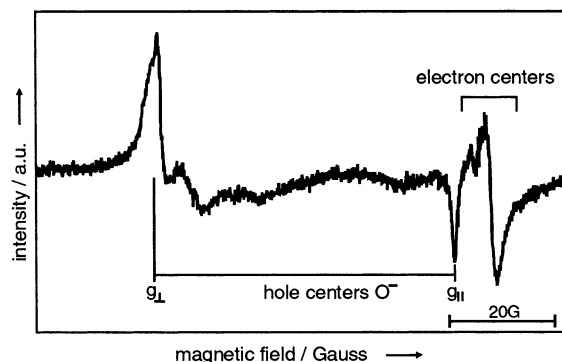

Figure 1. EPR spectrum of hole and electron centers generated by monochromatic irradiation (282 nm) of MgO powder at 77 K under dynamic vacuum conditions.
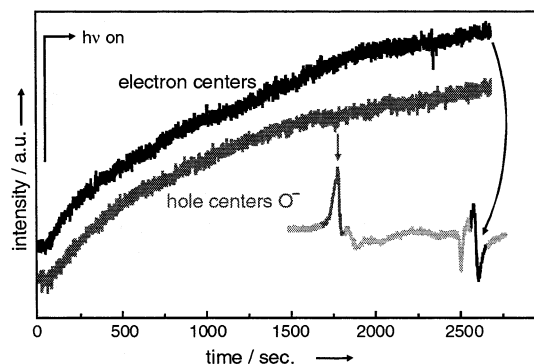

Figure 2. Time evolution of EPR signals of the hole (gray) and electron (black) centers during monochromatic irradiation (282 nm) at 77 K under dynamic vacuum condition (same result for irradiation at 237 nm).
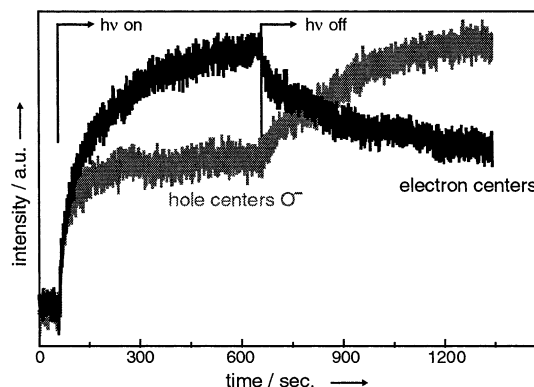

Figure 3. Polychromatic irradiation of MgO at 77 K under dynamic vacuum conditions. Time evolution of hole center (gray) and electron center (black) signals during irradiation (*hν* on) and dark reaction (*hν* off) phase.

was directed through interference filters (Acton Research Corp; peak wavelengths = 282 and 237 nm, respectively; fwhm: 40 nm; transmittance: 40%). Optical low-pass filters (Schott) with cutoff energies ranging from 1.5 to 3.9 eV (830−320 nm) were used for the post-irradiation experiments. The EPR sample cell was made of Suprasil quartz glass and was connected to an appropriate high vacuum pumping rack. It allowed thermal activation of the MgO sample at less than 10^{-5} mbar and UV irradiation under dynamic vacuum conditions. The EPR spectra were recorded using a Bruker EMX 10/12 spectrometer system in the X-band. The spectra were recorded at 77 K to avoid line broadening of the paramagnetic species. A total of 10 spectra were accumulated to obtain a sufficient signal-to-noise ratio. The time evolution of electron and hole center signals was observed in situ at fixed resonance magnetic field value for the respective EPR transitions during UV irradiation.

Results

1. Formation of Electron and Hole Centers. In this section, we compare the effects of two types of photoirradiation on MgO samples. First, we use a monochromatic irradiation at 282 nm (4.5 eV), which is much smaller than the bulk excitation energy and excites preferentially the different types of 3-coordinated oxygen anions (corner anions).[8,19] Next we use polychromatic irradiation in a wide spectral range and observe a dramatic difference in dynamics of the EPR signals of generated electron and hole centers.

1.1. Monochromatic Irradiation. The EPR spectrum of paramagnetic centers generated by the monochromatic irradiation (282 nm, 4.5 eV) of MgO powder at 77 K under dynamic vacuum conditions is shown in Figure 1. It has two main features attributed to electron and hole species arising from the photoinduced ionization of the low-coordinated (LC) surface oxygen anions.

One of the features with characteristic g matrix components ($g_\perp$ = 2.036 and $g_\parallel$ = 2.002) has been attributed to 3-coordinated O^- centers[11,29] (designated in the following as hole centers). The second signal feature with the *g* value slightly smaller than the free spin value (*g* = 1.998) has been attributed to electrons trapped at the surface.[22] In the following, this signal will be referred to as due to an electron center. The time evolution of both the hole and electron centers during the irradiation of the MgO sample was studied by monitoring their EPR signal maxima shown in Figure 2. Both signals emerge on a time scale of minutes and exhibit a 1:1 time correlation.

The broad line shape of the $g_\perp$ component of the hole center signal (Figure 1) suggests a distribution of different sites responsible for the envelope. In a previous study,[11] the hole

center feature has been deconvoluted into two signals attributed to 3-coordinated O^- sites with different local environments: a sharp signal component, $O^-[N'']$, due to a perfect cube corner site and a broader one, $O^-[N']$, due to a set of less regular corner sites. The abundance of the two signals, $O^-[N']$ and $O^-[N'']$, depends strongly on the excitation energy in the spectral interval between 200 and 300 nm. The abundance maxima observed by Diwald et al.[11] are at 230 nm (5.4 eV) and 270 nm (4.6 eV) and correspond to the maxima in the optical absorption spectrum attributed to 4- and 3-coordinated oxygen ions, respectively.[8] However, only 3-coordinated O^- hole centers have been detected. This suggests that excitons or holes initially produced at 4-coordinated oxygen sites are ultimately trapped at 3-coordinated surface sites.[11,15] Quite obviously also the signal components related to electron centers originate from more than one species. The deconvolution is, however, not feasible in an unambiguous form.

The monochromatic irradiation experiment was also repeated with higher energy photons of about 237 nm (5.4 eV). The result is almost identical to that obtained with the 282 nm (4.5 eV) light (Figure 2).

1.2. Polychromatic Irradiation. Irradiation of the MgO powder sample with polychromatic light produced by a 300 W Xe high-pressure lamp (200−900 nm) results in a very different dynamics of hole and electron center signals compared with those induced by the monochromatic 282 nm irradiation (Figures 2 and 3).

The signals due to the hole and electron centers grow at a much faster rate and exhibit different saturation behavior. Thus,

there is no time-correlated evolution of the g signal components of these centers (Figure 3).

In particular, during the irradiation period (60−600 s), the O^- signal clearly reaches a saturation level, whereas the electron center signal still increases monotonically with decreasing slope. After the irradiation was switched off (660 s), the O^- signal increases again, while the electron center signal decays.

The difference of the two signal patterns in Figures 2 and 3 is evidently related to the type of irradiation of the sample. The electron and hole center signals induced by the monochromatic light are clearly time-correlated (Figure 2). The virgin MgO powder after thermal treatment at 900 °C in high vacuum exhibits only two absorption bands in the spectral interval between 200 and 300 nm attributed to 3- and 4-coordinated surface oxygen anions, respectively. The rest of the near UV/vis spectral region does not demonstrate any measurable absorption. Therefore, the initial step of surface excitation during monochromatic and polychromatic irradiation should be the same. The dynamics presented in Figure 3 strongly suggests that other photons, which are present only in the polychromatic radiation, are likely to be the main cause of the observed difference.

In fact, the experiment in Figure 3 (irradiation in the spectral interval 200−900 nm) differs from that in Figure 2 (irradiation at 282 and 237 nm) only by the presence of low energy photons. Therefore, we conclude that the additional processes invoked by the polychromatic irradiation are due to photons of lower energies in the range of 300−900 nm.

To shed some light on the effect of these photons on the UV generated electron and hole centers, we carried out additional experiments with specific spectral intervals of low energy radiation.

2. Effect of Low Energy Irradiation. *2.1. Electron Centers.* To determine the influence of the irradiation on the stability of the electron centers a population of the surface electron centers was generated by irradiation of the MgO powder with monochromatic light of 282 nm (4.5 eV) as described in section 1.1. Then the sample was additionally post-irradiated with polychromatic light and the intensity of the EPR signal of electron centers was monitored. Low energy irradiation was provided using the original 300 W Xe lamp with an optical low pass filter in the optical beam path. The cutoff energies of the optical filters range from 830 (1.5 eV) to 320 nm (3.9 eV). Figure 4 shows the dependence of the EPR signal intensity on the cutoff energy of the optical filters.

Photons with energies up to 1.8 eV have no significant influence on the signal intensity. Increasing the photon energy above 2 eV induces a reduction of the intensity of the electron center signal. This decrease of the signal indicates a transformation of the paramagnetic centers to diamagnetic ones. The sharp decrease of the signal intensity at cutoff energies between 2.0 and 2.5 eV corresponds to ionization of approximately 80% of electron centers. The remaining 20% survive up to cutoff energies of 3.9 eV.

2.2. Hole Centers. To separate the effect of post-irradiation on the hole centers (3-coordinated O^- ions) from that on the electron centers the latter ones were bleached using the following procedure. (i) Both the electron and hole centers were first generated by irradiating the MgO sample with monochromatic light as described in section 2.1. (ii) Immediately after the end of irradiation, all electron centers were bleached with molecular oxygen, which resulted in the formation of superoxide O_2^- ions.[30] (iii) The residual molecular oxygen was pumped off until the original vacuum level is restored, the sample was cooled to

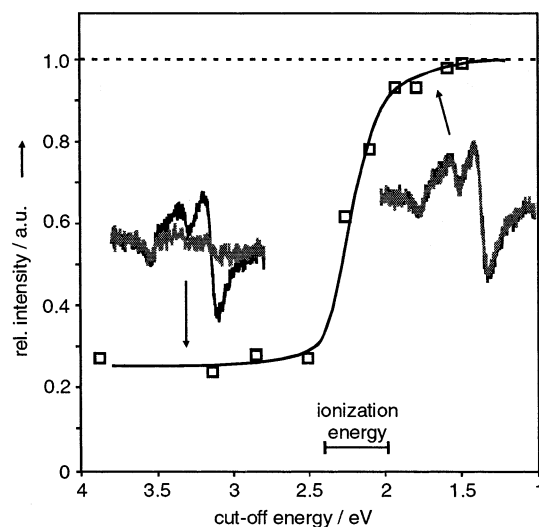**Figure 4.** EPR signal intensity (□) of the electron centers after post-irradiation using optical filters of different cutoff energies. The dashed line corresponds to the initial concentration of electron centers generated by 282 nm irradiation. The black and the gray curves represent the EPR signals before and after post-irradiation, respectively.
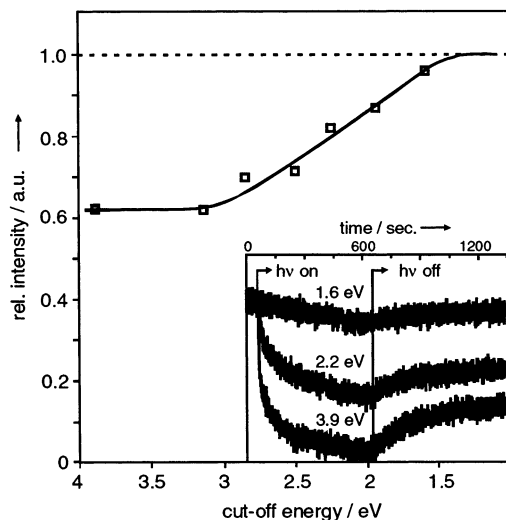

Figure 5. EPR signal intensity (□) of the hole centers (O^-) after post-irradiation using optical filters of different cutoff energies. The dashed line corresponds to the initial concentration of hole centers generated by 282 nm irradiation. The inset shows the time evolution of the EPR signal during (*hν* on) and after (*hν* off) post-irradiation at different cutoff energies.

77 K and irradiated with a polychromatic light using the same filters as described in section 2.1. The intensities of the hole and electron centers as well as that of the superoxide anions were monitored during the post-irradiation described in point iii. We checked that no measurable concentration of paramagnetic electron centers was produced during the polychromatic irradiation. The signal intensity of the superoxide anion species produced by bleaching of electron centers with molecular oxygen remained unchanged during these irradiation experiments. On the other hand, the hole center signal intensity demonstrated a clear dependence on the cutoff energy as shown in Figure 5. In the inset, the evolution of the EPR signal intensity of the hole centers with the time of irradiation is displayed for selected cutoff energies. A reduction of the hole center signal is observed which is higher for larger cutoff energies. Switching off the radiation source (660 s, *hν* off) induces a partial recovery of the hole centers but the initial intensity could not be reached

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in any experiment. The decrease of the hole center signal intensity is almost linear up to a cutoff energy of 3.0 eV where the hole recovery rate reaches 60%. Further increase of the cutoff energy to 3.9 eV does not affect the time evolution and recovery rate of the signal.

Discussion

According to Ito et al.,[22] monochromatic UV irradiation (253 nm) of MgO in vacuo at 77 K leads to the formation of hole and electron centers stabilized on the MgO surface. The same effect is observed in this work (Figure 1) for the lower energy photons (282 nm). On the other hand, this excitation induces photoluminescence[14] with a lifetime much shorter than the recombination time (milliseconds)[21] of the electron and hole centers. The observed formation of a considerable amount of hole and electron centers can be understood if one assumes a sequential absorption of two photons where the absorption of the first photon leads to the formation of a transient state—an exciton at a 3-coordinated anion site—and absorption of the second photon removes the excited electron which either becomes trapped at some electron trapping center or leaves the sample.

To test this hypothesis, we carried out embedded cluster density functional theory (DFT) calculations of the ionization energies of the relaxed triplet exciton excited at a corner site of the MgO surface. The full setup of these calculations is described in refs 26, 27, and 31. The calculated ionization energies are about 2 eV, which suggests that thermal ionization of corner excitons excited by 282 nm photons is unlikely and supports the mechanism involving secondary photoexcitation.

A further evidence of close interconnection between the hole and electron centers is given by studying the time evolution of the EPR signal of both centers under the continuous irradiation. In the case of the monochromatic irradiation (Figure 2), we observed a 1:1 correlation between hole center and electron center formation which strongly suggests that these centers are created in the same process. However, this 1:1 correlation vanishes if a polychromatic source with a radiation spectrum of 200−900 nm is used. This different behavior can be understood if we assume the existence of a number of other photoinduced processes, complementary to the sequential absorption of two photons described above.

The results of the previous section strongly support this assumption and suggest that the observed saturation of the electron and hole center signals (Figure 3) is due to a competition between a series of photoinduced and thermally activated processes resulting in formation and recombination of these centers. Some of the possible processes are listed below.

(i) Photostimulated recombination: electron traps can be ionized in the course of continuous irradiation and the released electrons can recombine with hole centers thus restoring the original electronic structure of the system.

(ii) Coulomb blockade: a hole localized at a 3-coordinated anion site or at a step can make the formation of another hole nearby less likely. This also makes the localization of two holes at the same site energetically unfavorable.

(iii) Excitation of localized holes into the valence band: if the kinetic energy of the excited hole is large enough, it can travel far from its original site and become trapped at impurities or lattice irregularities with no distinct EPR signal.

(iv) Delocalization of the holes excited to the valence band: delocalized holes become EPR invisible.

The following processes might be responsible for the dark reaction.

(v) Generation of double hole centers (3-coordinated O^0 species): these centers will readily trap an electron and convert to O^- after the irradiation is switched off.

(vi) Release of holes from transient traps and their localization at the 3-coordinated O^{2-} sites.

(vii) Decay of a significant proportion of the electron centers via thermal ionization or electron tunneling.

To narrow down the range of processes induced by the low-energy photons we note that mechanisms i and ii are also present in the case of monochromatic irradiation. Formation of double hole centers suggested in mechanism v is unlikely due to the electrostatic repulsion of the holes. We also note that mechanism iv is expected to have a minor effect because the free holes excited to the valence band should localize on a time scale much shorter than the time scale of the back reaction.

The results presented in Figure 4 shed some light on the nature of paramagnetic electron centers. The surface nature of these centers is evidenced by their complete conversion to superoxide anion species after reaction with molecular oxygen at room temperature. Bare surface anion vacancies were traditionally considered as potential electron traps.[10] Recent calculations[31] demonstrated, however, that the ionization energy of paramagnetic surface anion vacancies with one electron is about 5.6 eV (F^+ centers in surface terrace sites). On the other hand, a sharp decrease of the EPR signal intensity of paramagnetic electron centers observed during post-irradiation at photon energies of about 2.3 eV (Figure 4) corresponds to the ionization of approximately 80% of these centers. A simultaneous decrease of the hole center signal indicates, that electrons released from electron traps get trapped by hole centers. Thus, most of the paramagnetic electron centers originating from UV irradiation in vacuo, as discussed here, have much smaller ionization energies than F^+ centers at surface terrace sites. This result corroborates extremely well with recent theoretical predictions of the ionization energies of electrons trapped at other structural defects, such as divacancies and Mg corner and kink sites. These defects are shallow electron traps with the calculated ionization energies of about 1−2 eV.[25−27]

In our experiments we found a decrease of the EPR signal intensity of hole centers during the post-irradiation at cutoff energies of up to 3 eV (Figure 5). This can be explained by the excitation of the localized holes from 3-coordinated O^- sites to the valence band. Our DFT calculations using the embedded cluster model described in refs 26, 27, and 31 have shown that the minimum hole excitation energy required to transfer an electron from the valence band into the unoccupied state of the hole at a 3-coordinated anion site is 1−1.5 eV, depending on the local atomic structure of the site. Thus, the larger the cutoff energy of the filter, the higher the maximum kinetic energy acquired by the excited holes. Consequently, these holes can travel larger distances and have more possibilities to become trapped at hole traps deeper inside the powder. The net effect of such process is a lower hole center recovery rate for larger cutoff energies, which is in agreement with our results (see inset in Figure 5).

These results allow us to suggest a possible mechanism of the time evolution of the EPR signals of O^- and electron centers induced by mono- and polychromatic irradiation (Figures 2 and 3). In the case of polychromatic irradiation, the formation of 3-coordinated O^- centers via sequential absorption of two photons and formation of electron centers via electron trapping is also accompanied by the excitation of the holes from the 3-coordinated O^- sites to the valence band and their subsequent trapping at unspecified hole traps. (We comment on the nature

of these traps below.) These traps should be present in significant amount to provide fast saturation of the 3-coordinated O^- signal, but they have no distinct EPR feature. When the irradiation is switched off, some of the holes released from the unspecified hole traps localize at the 3-coordinated O^{2-} sites which results in the growth of the O^- signal (Figure 3). Other released holes recombine with the electrons from the electron centers thus reducing their population. In the case of the monochromatic irradiation, the 4.5 eV (or 5.4 eV) photons cannot excite the holes from the 3-coordinated O^- sites to the valence band. Thus, all holes remain localized at the 3-coordinated anions and the 1:1 correlation between the hole and electron centers is preserved.

The model described above relies on the assumption that a significant concentration of defects capable of temporarily trapping holes and electrons in shallow and paramagnetically inactive states is present in our samples. Transition metal ions like Mn, Cr, or Fe, which are present in MgO as impurities in minor concentrations, would be able to serve as transient hole traps. However, no significant changes in the EPR spectra of Mn and Cr centers have been observed which would indicate a change in their valence state during the polychromatic irradiation. An EPR signal corresponding to Fe could not be observed in the present study, which might be due to the fast spin–lattice relaxation time of Fe at 77 K. A definite exclusion of transition metal ions as hole traps may be possible on the basis of variable temperature experiments. Other abundant defects, which may play an important role in electron and hole trapping processes, are interfaces between different powder particles. Clearly, the nature of these defects requires further studies.

The simple model described above may need to be extended further to include other processes necessary to fully explain the observed experimental results. However, the results presented in this paper give a clear indication that our samples contain various types of electron and hole traps some of which have a optical depth of about 2–3 eV, but some others are shallow enough that they can be thermally ionized even at low temperatures leading to dark reactions. They contribute to better understanding of photoinduced reactions in MgO samples and can be useful for the understanding of similar processes in other oxides, such as ZrO_2 and TiO_2.

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