In situ XPS analysis of various iron oxide films grown by NO$_2$-assisted molecular-beam epitaxy

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We report on a systematic analysis of x-ray photoelectron spectroscopy (XPS) core- and valence-level spectra of clean and well-characterized iron oxide films, i.e., $\alpha$-Fe$_2$O$_3$, $\gamma$-Fe$_2$O$_3$, Fe$_{1-x}$O, and Fe$_3$O$_4$. All iron oxide films were prepared epitaxially by NO$_2$-assisted molecular-beam epitaxy on single crystalline MgO(100) and $\alpha$-Al$_2$O$_3$(0001) substrates. The phase and stoichiometry of the films were controlled precisely by adjusting the NO$_2$ pressure during growth. The XPS spectrum of each oxide clearly showed satellite structures. These satellite structures were simulated using a cluster-model calculation, which could well reproduce the observed structures by considering the systematic changes in both the Fe 3$d$ to O 2$p$ hybridization and the $d$-$d$ electron-correlation energy. The small difference in the satellite structures between $\alpha$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$ resulted mainly from changes in the Fe-O hybridization parameters, suggesting an increased covalency in $\gamma$-Fe$_2$O$_3$ compared to $\alpha$-Fe$_2$O$_3$. With increasing reduction in the $\gamma$-Fe$_2$O$_3$-Fe$_3$O$_4$ system, the satellite structures in XPS became unresolved. This was not only due to the formation of Fe$^{2+}$ ions, but also to nonhomogeneous changes in the hybridization parameters between octahedral and tetrahedral Fe$^{3+}$ ions.

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I. INTRODUCTION

The electronic structure of iron oxides has been the subject of many experimental and theoretical studies. Theoretical calculations of iron oxides have been performed in order to get information about the electronic structure and the magnetic properties. In particular, the theoretical calculation of the electronic structure of iron oxides has been performed in order to understand the magnetic properties of iron oxides.

The electronic structure of iron oxides is important for many applications, such as catalysts and magnetic devices. Iron oxides are materials of great importance in many technological applications such as catalysts and magnetic devices. Furthermore, they are products in the corrosion process of steel.

To obtain information about the electronic structure of solids, x-ray photoelectron spectroscopy (XPS) is one of the most powerful tools. Despite extensive XPS investigations of various iron oxides, our knowledge of the electronic structure is still not yet achieved. The difficulty in interpreting XPS spectra arises from both theoretical and experimental facts. The theoretical difficulty comes from the correlation effects among the Fe 3$d$ electrons and the hybridization between the Fe 3$d$ and the ligand O 2$p$ states, which give complicated multiplet structures in the spectra. The experimental one is associated with controlling the stoichiometry of iron oxides and with preparing clean and well-characterized surfaces. XPS spectra are easily influenced by the presence of contaminations such as water and hydrocarbons on the surface.

The possibility to grow well-crystallized iron-oxide films by molecular beam epitaxy (MBE) has been widely demonstrated. In the MBE growth of iron-oxide films, the use of NO$_2$ as a source of oxygen allows the formation of almost all iron oxide phases in the Fe-O system. The stoichiometry of the oxides can be controlled precisely by adjusting the flux of NO$_2$. Depending on the NO$_2$ pressure during the growth, epitaxial layers of stoichiometric Fe$_3$O$_4$ (magnetite) or all phases of nonstoichiometric Fe$_{1-x}$O$_4$ up to the completely oxidized one, i.e., stoichiometric $\gamma$-Fe$_2$O$_3$ (magnetite), can be formed on cubic MgO(100) substrates, while on hexagonal $\alpha$-Al$_2$O$_3$ substrates in combination with the high NO$_2$ pressure, epitaxial layers of stoichiometric $\alpha$-Fe$_2$O$_3$ (hematite) are formed. Therefore, we will report here on in situ XPS measurements on clean and well-characterized surfaces of various iron oxide films, prepared by the NO$_2$-assisted MBE technique.

The crystal structures of these oxides are normally described as structures based upon a framework of close-packed (cp) oxygen sublattices. Hematite is an antiferromagnetic insulator with a corundum structure, in which Fe$^{3+}$ ions are octahedrally coordinated by hexagonal cp O$^{2-}$ ions. Magnetite, maghemite, and their intermediate compound, Fe$_{x_1}$O$_{4-x}$, are ferrimagnetic materials having an inverse spinel structure with cubic cp O$^{2-}$ ions. The usual formula representation of magnetite is [Fe$^{3+}$]$_{100}$[Fe$^{2+}$Fe$^{3+}$]$_{100}$O$_{400}$, indicating that the Fe$^{3+}$ ions occupy octahedral sites and that the Fe$^{3+}$ ions are distributed evenly over octahedral and tetrahedral sites. At room temperature, Fe$_3$O$_4$ has a high conductivity because of a rapid electron hopping between octahedral Fe$^{3+}$ and Fe$^{2+}$ ions. Oxidizing Fe$_2$O$_3$ to Fe$_{1-x}$O$_x$, the Fe$^{2+}$ ions in the octahedral sites are replaced with vacancies and Fe$^{3+}$ ions as [Fe$^{3+}$]$_{100}$[Fe$_{1-x}$O$_{4-x}$]$_{100}$O$_{400}$. $\gamma$-Fe$_2$O$_3$, which is the insulator, has the highest oxidized structure of [Fe$^{3+}$]$_{100}$[Fe$_{5/3}$Fe$^{3+}$O$_{4}$].
It is well known that XPS spectra of iron oxides exhibit so-called shake-up satellite structures. These satellite structures, which are very sensitive to the electronic structure of the compounds, are frequently used as fingerprints to identify the iron oxide phases. Theoretically, the cluster-model calculation can successfully be applied to reproduce the structures in XPS spectra of 3\textit{d} transition compounds.\textsuperscript{6,21–24} The multiplet interaction of the core hole created in the photoemission process with the 3\textit{d} electrons is strong enough to redistribute the final-state electron configurations. Also, the configuration interaction produced by charge transfer from the ligand 2\textit{p} orbitals to the metal 3\textit{d} states influences the shape of the spectrum. In this paper, we present the systematic study of XPS Fe 2\textit{p} core-level and valence-band spectra of various epitaxial iron-oxide films, based upon this theory.

### II. EXPERIMENT

To prepare various iron oxides as epitaxial films, we used an ultrahigh vacuum (UHV) system comprising both MBE and XPS chambers. The base pressure of the MBE chamber was 1×10\textsuperscript{-8} Pa. Before deposition, a single-crystalline substrate of MgO(100) or \(\alpha\)-Al\textsubscript{2}O\textsubscript{3}(0001) with dimensions of 10×10×0.3–1.0 mm\textsuperscript{3} was annealed for 12 h at 923 K under an O\textsubscript{2} pressure of 1×10\textsuperscript{-4} Pa, in order to remove hydrocarbon contaminations from the surface. Crystalline order and cleanliness of the substrate surface were checked with low-energy electron diffraction (LEED), reflection high-energy electron diffraction (RHEED), Auger electron spectroscopy, and XPS.

During deposition, Fe metal was evaporated from a Knudsen cell onto the substrates, with the simultaneous oxidation by an NO\textsubscript{2} flux coming from a small buffer volume. The flux was regulated by adjusting the pressure in the buffer volume, and therewith the degree of oxidation could be precisely controlled. By using a small flux of the more reactive NO\textsubscript{2}, instead of conventional O\textsubscript{2}, the MBE chamber could maintain a low-background pressure (<1×10\textsuperscript{-5} Pa) during deposition. The substrate temperature was fixed at 623 K for \(\alpha\)-Fe\textsubscript{2}O\textsubscript{3} films on \(\alpha\)-Al\textsubscript{2}O\textsubscript{3} or at 523 K for Fe\textsubscript{3}O\textsubscript{4}, Fe\textsubscript{2−\textit{x}}O\textsubscript{\textit{x}}, and \(\gamma\)-Fe\textsubscript{2}O\textsubscript{3} films on MgO. All films had a thickness of about 250 Å, which was monitored by counting the number of RHEED intensity oscillations and by a quartz-crystal oscillator. The \(\delta\) values of Fe\textsubscript{3−\textit{x}}O\textsubscript{\textit{x}} films on MgO were determined \textit{ex situ} by conversion-electron Mössbauer spectroscopy (CEMS). Figures 1(a) and 1(b) are typical CEMS spectra of Fe\textsubscript{3−\textit{x}}O\textsubscript{\textit{x}} films prepared at NO\textsubscript{2} buffer volume pressure of 0.166 and 1.33 Pa, respectively. The spectrum at NO\textsubscript{2}=0.166 Pa corresponds to nearly stoichiometric Fe\textsubscript{2}O\textsubscript{3}, while the spectrum at 1.33 Pa was consistent with the one for stoichiometric \(\gamma\)-Fe\textsubscript{2}O\textsubscript{3}. The \(\delta\) values of all Fe\textsubscript{3−\textit{x}}O\textsubscript{\textit{x}} sample films are summarized in Table I as a function of the NO\textsubscript{2} pressure. We emphasize here that the NO\textsubscript{2}-assisted MBE technique could successfully induce the formation of a stoichiometric film of the metastable spinel oxide, \(\gamma\)-Fe\textsubscript{2}O\textsubscript{3}. Details of the thin-film growth process, stoichiometry determination, and crystalline structure of these films were already reported in Refs. 15 and 18–20.

After deposition, the sample films were immediately transferred from the MBE chamber to the XPS chamber under UHV conditions. XPS was performed by using non-monochromatic Al K\textalpha\ radiation (\(h\nu=1486.6\) eV) and a VG Clam II hemispherical electron-energy analyzer. The pressure of the XPS chamber during the measurement was 5×10\textsuperscript{-10} Pa, and the instrumental broadening measured at the Ag Fermi edge was estimated to be about 1 eV. Some sample films showed charging (<8 eV) in XPS spectra because of their insulator nature. The binding energies were corrected for the charging effect by assuming a constant binding energy for the O 1\textalpha\ peak of 530.1 eV. All spectra were corrected by subtracting a Shirley-type background,\textsuperscript{25} after subtracting the satellites due to the K\textalpha\ components of the incident x-rays. The XPS O 1\textalpha\ spectra of the sample films, shown in Fig. 2, all had a nearly identical single-line profile. The symmetric peak shape without low-intensity side bands proves the cleanliness of the surfaces.

### III. CALCULATION METHOD

In the cluster model approach to simulate XPS spectra of 3\textit{d} transition-metal compounds, the parameters of the Coulomb interaction (\(Q\)) between the core hole (\(\zeta\)) and the 3\textit{d} electron, the correlation energy (\(U\)) between the 3\textit{d} electrons, the ligand 2\textit{p} to the metal 3\textit{d} charge-transfer energy (\(\Delta\)), and the ligand 2\textit{p} to the metal 3\textit{d} hybridization energy (\(T\)) are explicitly taken into account.\textsuperscript{21,24} The ground-state electron configuration is given by a linear combination of 3\textit{d}\textsuperscript{\textit{n}}, 3\textit{d}\textsuperscript{\textit{n}+1}\textit{L}, and 3\textit{d}\textsuperscript{\textit{n}+2}\textit{L}\textsuperscript{2} up to 3\textit{d}\textsuperscript{\textit{m}+10}\textit{L}\textsuperscript{10−\textit{n}}, where \(\textit{n}\) and \(\textit{L}\) denote the number of 3\textit{d} electrons and the ligand hole on

<table>
<thead>
<tr>
<th>NO\textsubscript{2} buffer volume pressure (Pa)</th>
<th>(\delta) values in Fe\textsubscript{3−\textit{x}}O\textsubscript{\textit{x}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.166</td>
<td>0.013±0.004</td>
</tr>
<tr>
<td>0.233</td>
<td>0.030±0.004</td>
</tr>
<tr>
<td>0.333</td>
<td>0.251±0.007</td>
</tr>
<tr>
<td>0.400</td>
<td>0.270±0.006</td>
</tr>
<tr>
<td>0.666</td>
<td>0.284±0.008</td>
</tr>
<tr>
<td>1.33</td>
<td>0.333</td>
</tr>
</tbody>
</table>

Figure 1 shows typical CEMS spectra of Fe\textsubscript{3−\textit{x}}O\textsubscript{\textit{x}} films grown on MgO(100) at NO\textsubscript{2} buffer volume pressures of (a) 0.166 Pa and (b) 1.33 Pa.
ligand O$^{2-}$ ions, respectively. In our calculations, the higher energy terms beyond the first three configurations were neglected. In the same way, the final-state configuration in XPS is given by a linear combination of $\zeta 3d^n$, $\zeta 3d^{n+1}L$, and $\zeta 3d^{n+2}L^2$. The core-potential lowers the $3d^{n+1}L$ and $3d^{n+2}L^2$ states by $Q$ and $2Q$, respectively, compared to the $3d^n$ state, which causes a different ordering of final-state levels from initial ones. This is the reason for the strong satellite structure in XPS spectra.

In the simplest crystal-field picture, the $3d$ levels in octahedral symmetry ($O_h$) are split into two $e_g$ and three $t_{2g}$ orbitals, separated by $10Dq$. Each orbital gives a different $p-d$ hybridization energy, as $Te_g = \sqrt{3}(pd\sigma)$ or $Tt_{2g} = 2(pd\sigma)$, defined by the Slater-Koster transfer integrals. The tetrahedral symmetry ($T_d$) gives, compared to the $O_h$ symmetry, an inverted crystal-field splitting. Here, the two $e$ orbitals are lower in energy than the three $t_2$ orbitals. The $p-d$ hybridization for each orbital is defined as $Te = 2/3 \sqrt{6}(pd\pi)$ or $Tt_{2g} = 2/3\sqrt{2}(pd\pi)$ or $2/3\sqrt{3}(pd\sigma)$. In the present calculation, $\Delta$ and $U$ were defined with respect to the center of gravity of the configuration. Only three parameters of $\Delta$, $U$, and $Te(\sigma)$ were treated as adjustable parameters for simplicity. The anisotropy in hybridization was taken into account, adopting the empirical relation $Te_g = -2Tt_{2g}$ and $Te = -1/2 Tt_{2g}$. In the XPS Fe 3$d$ valence-band spectra, the 3$d$ electron hole is created in the Fe 3$d$ valence shell. The Coulomb interaction between the 3$d$ valence hole and the 3$d$ electron was considered equal to $U$. While in the XPS Fe 2$p$ core-level spectra, the Coulomb interaction ($Q$) was assumed to be slightly (0.5 eV) larger than $U$. Because a full-multiplet interatomic charge-transfer model approves the larger $U$ value than that the conventional relation of $U = 0.8Q$ expected, which is originally proposed by a pure charge-transfer model. If we adopt the relation of $U = 0.8Q$, we could not reproduce the XPS Fe 3$d$ valence-band and Fe 2$p$ core-level spectra simultaneously by using the same parameter values. The value of $10Dq$ is affected by both the ionic and the covalent contribution. The latter can be estimated from the short-range model parameters as $10Dq(cov)$.

FIG. 2. XPS O 1$s$ core-level spectra of various iron-oxide films prepared by the NO$_2$-assisted MBE technique. The NO$_2$ buffer volume pressures during deposition are indicated in each spectrum.

FIG. 3. Observed (a) and simulated (b) XPS Fe 2$p$ core-level spectra of an $\alpha$-Fe$_2$O$_3$ film on $\alpha$-Al$_2$O$_3$. The parameter values used for the simulation are listed in Table II.

$$= \sqrt{\Delta^2 + 4Te_g^2} - \sqrt{\Delta^2 + 4Tt_{2g}^2}.$$ The former was fixed to $10Dq(\text{ion}) = 0.5$ eV because it had little effect on the XPS spectral shape. The Slater integrals were scaled down to 85% of the ionic Hartree-Fock-Slater calculation.

IV. RESULTS AND DISCUSSION

A. $\alpha$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$ films

Ferric oxides are polymorphic, i.e., they occur as $\alpha$-Fe$_2$O$_3$ with a corundum structure and $\gamma$-Fe$_2$O$_3$ with a deficient spinel structure. Despite the large differences in their crystal structures, the XPS Fe 2$p$ core-level spectra of $\alpha$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$ are known to be almost identical with each other. Figure 3(a) shows the XPS Fe 2$p$ spectrum of an $\alpha$-Fe$_2$O$_3$ film on $\alpha$-Al$_2$O$_3$(0001), while the spectrum of a $\gamma$-Fe$_2$O$_3$ film on MgO(100) is shown in Fig. 4(a). The formation of stoichiometric $\gamma$-Fe$_2$O$_3$ without any Fe$^{2+}$ components was confirmed by CEMS, RHEED and LEED. The Fe 2$p_{3/2}$ and 2$p_{1/2}$ main peaks of both films are clearly accompanied by satellite structures on their high binding-energy side, at about 8 eV. The binding energy of about 711 eV for the Fe 2$p_{3/2}$

FIG. 4. Observed (a) and simulated (b) XPS Fe 2$p$ core-level spectra of a $\gamma$-Fe$_2$O$_3$(100) film on MgO(100). The simulated spectrum labeled “Total” is obtained by a weighted summation of the octahedral and tetrahedral Fe$^{3+}$ components. The parameter values used for the simulation are listed in Table II.
TABLE II. Spectral parameters of the XPS Fe 2p 1/2 core-level spectra of α-Fe 2O 3 and γ-Fe 2O 3 films shown in Figs. 3(a) and 4(a), respectively. Tabulated are the binding energy of the 2p 3/2 peak maximum (BE), the intensity ratio of the satellite to the main peak (I s/I M), and the separation between them (δE).

<table>
<thead>
<tr>
<th>Compound</th>
<th>BE (eV)</th>
<th>I s/I M</th>
<th>δE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Fe 2O 3</td>
<td>710.9</td>
<td>0.473</td>
<td>8.1</td>
</tr>
<tr>
<td>γ-Fe 2O 3</td>
<td>710.7</td>
<td>0.446</td>
<td>8.2</td>
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</table>

A main peak is consistent with typical values for the ferric oxides reported in the literature. The observed spectral parameters of the 2p 3/2 peaks for both films are listed in Table II. We find that the Fe 2p spectrum of the clean Fe 2O 3 film have two remarkable features compared with that of the clean α-Fe 2O 3, and both are quite reproducible: (i) the intensity of the satellite peak is reduced, and (ii) the 2p 3/2 main peak is slightly shifted to lower binding energy.

In the case of α-Fe 2O 3, all the Fe 3+ ions occupy octahedral sites. So, the calculation of the XPS Fe 2p core-level spectrum for α-Fe 2O 3 involved only one FeO 6 cluster. Figure 3(b) shows a simulated XPS Fe 2p spectrum by using the parameter values listed in Table II. The simulated spectrum well reproduces the satellite structures in the observed spectrum. The parameter values used agree well with the values reported by other groups, as measured with XPS (Ref. 6) or x-ray absorption spectroscopy. It should be noticed that “Δ eff” and “U eff” as used in the so-called Zaanen-Sawatzky-Allen diagram are defined with respect to the lowest energy configuration by both the multiplet splitting and the crystal-field splitting. The effective charge-transfer energy Δ eff and the 3d-3d correlation energy U eff have the following relations with “Δ” and “U” used in our calculation, i.e., Δ eff = Δ + 2δ 6 − δ 6+1 − δ 6−1 and U eff = U + 2δ 6 − δ 6+1 − δ 6−1, respectively, where δ n denotes the energy difference between the center of gravity and the lowest energy for the d n configuration. Depending on the relative values of U eff and Δ eff, the oxides are classified as a semiconductor, a semiconductor-insulator, or a charge-transfer insulator (U eff > Δ eff). The parameter values of Table II are plotted in the ZSA diagram shown in Fig. 5. The electronic structure in the α-Fe 2O 3 film clearly indicates that it is a charge-transfer insulator as reported previously.

TABLE III. Parameter values (Δ, Tε(ε), T 1/2(ε), U, and Q) of various iron oxides used for the cluster calculation of the XPS Fe 2p spectra. The last column is the iron-to-oxygen mean distance (r) of each site reported for bulk crystals.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sites</th>
<th>Δ (eV)</th>
<th>Tε(ε) (eV)</th>
<th>T 1/2(ε) (eV)</th>
<th>U (eV)</th>
<th>Q (eV)</th>
<th>r (Å)</th>
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<tbody>
<tr>
<td>α-Fe 2O 3</td>
<td>FeO 6 3+</td>
<td>2.0</td>
<td>2.6</td>
<td>−1.3</td>
<td>7.5</td>
<td>8.0</td>
<td>1.99</td>
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<tr>
<td>γ-Fe 2O 3</td>
<td>FeO 6 3+</td>
<td>2.0</td>
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<td></td>
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</table>
not reasonably reproduce the simultaneous changes in both the satellite intensities and the positions. Therefore, we conclude that the decreased satellite intensity of $\gamma$-Fe$_2$O$_3$ compared to $\alpha$-Fe$_2$O$_3$ is mainly caused by an increase in $T$. However, the Harrison’s relation states that $T$ varies with the interatomic distance as $r^{-3.5}$. So one expects, on the contrary, a decrease in $T$ of $\gamma$-Fe$_2$O$_3$ because the octahedral Fe-O distance in bulk $\gamma$-Fe$_2$O$_3$ is about 2% larger than that in bulk $\alpha$-Fe$_2$O$_3$. Therefore, our experimental results suggest that the Harrison’s relations could not be applied rigidly on these systems because the crystal structures of $\gamma$-Fe$_2$O$_3$ and $\alpha$-Fe$_2$O$_3$ are very different. Another explanation might be that the lattice mismatch between the film and substrate induces anisotropic strains at the interface, leading to a change in the interatomic distances in thin films. Nevertheless, the increase in $T$ of the $\gamma$-Fe$_2$O$_3$ film suggests that the Fe-O bonds in $\gamma$-Fe$_2$O$_3$ are more covalent than those in $\alpha$-Fe$_2$O$_3$, causing the intra-atomic Coulomb energies of $\gamma$-Fe$_2$O$_3$ and $U$ to be screened by the density of polarizable bonds.

The increasing covalency could shift the binding energy of the XPS Fe 2$p$ levels. This is a second reason for the lowered binding energy of the Fe 2$p_{3/2}$ main peak for $\gamma$-Fe$_2$O$_3$.

The $p$-$d$ hybridization also influences the satellite positions. The separation between the main and the satellite peaks is approximately given by $\delta E = [(\Delta - Q)^2 + 4T^2]^{1/2}$. The increase in $T$ of $\gamma$-Fe$_2$O$_3$ as discussed above makes $\delta E$ larger, while the decrease in $Q$ makes it smaller when $\Delta < Q$. These two effects cancel each other almost out and the simulated parameters of $\gamma$-Fe$_2$O$_3$ give a very small decrease in $\delta E$ for the octahedral Fe$^{3+}$ ions. On the other hand, the spectrum for the tetrahedral Fe$^{3+}$ has satellite positions with larger $\delta E$. Therefore, the XPS Fe 2$p$ core-level spectrum of $\gamma$-Fe$_2$O$_3$ contains almost the same satellite positions, but with smaller intensities compared to $\alpha$-Fe$_2$O$_3$.

Figures 6(a) and 7(a) show the observed XPS spectra of the valence-band region of $\alpha$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$ films, respectively. Both spectra consist of a main band (0–10 eV), a satellite band (10–17 eV) and the O 2$s$ level (21.5 eV). The main band in both spectra seems to have a three-peak structure with maxima at about 2.7, 4.9, and 7.2 eV, which is in good agreement with the valence-band structures of the corresponding bulk crystals. The most remarkable difference between $\alpha$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$ is the intensity of the first peak in the main band at about 2.7 eV. The integrated intensity of the valence-band region (−2.5–17.0 eV) normalized on the O 2$s$ intensity is plotted in Figure 8 for the various iron oxide films. It is noticeable that the valence-band intensity of $\alpha$-Fe$_2$O$_3$ is slightly smaller than that of $\gamma$-Fe$_2$O$_3$. This should relate in some way to the difference in the number of valence states and suggests a more covalent nature of $\gamma$-Fe$_2$O$_3$ compared to $\alpha$-Fe$_2$O$_3$. The valence-band spectra are mainly comprised of the Fe 3$d$ and the O 2$p$ levels. The increased covalency of the Fe$^{3+}$O$^{2-}$ bonds should move the electron population from the O 2$p$ derived states to the Fe 3$d$ derived states. Furthermore, the photoemission cross section of Fe 3$d$ is much larger than that of O 2$p$. Taking this into account, it is concluded that the Fe-O bonds in $\gamma$-Fe$_2$O$_3$ are more covalent than those in $\alpha$-Fe$_2$O$_3$, in agreement with the larger Fe 3$d$-O 2$p$ hybridization as discussed above.

The same parameter values of $\Delta$, $T$, and $U$ derived from the XPS Fe 2$p$ core-level spectra (see Table III) were used for the simulation of the XPS Fe 3$d$ valence-band spectra. The effects of the configuration-dependent hybridization,
which should bring about a small difference in these parameter values between the XPS Fe 2p and 3d spectra, were ignored.\textsuperscript{35} The simulated spectra shown in Figs. 6(b) and 7(b) reproduce well the satellite structures for both α-Fe\textsubscript{2}O\textsubscript{3} and γ-Fe\textsubscript{2}O\textsubscript{3} films. It should be noticed again that the Fe 3d derived main bands are contaminated by a large contribution from unhybridized O 2p states,\textsuperscript{8,8} which are left unconsidered in the present calculation. Lad and Henrich reported that the O 2p emission exhibited a single broad maximum between 2 and 8 eV, and that the peak shape was essentially identical in each of the various iron oxides.\textsuperscript{8} So, the differences in the main band structures between α-Fe\textsubscript{2}O\textsubscript{3} and γ-Fe\textsubscript{2}O\textsubscript{3} should mainly result from changes in the Fe 3d derived states. The calculated spectrum for the tetrahedral Fe\textsuperscript{3+} ions gives a large intensity at lower energies. Thus, we conclude that the tetrahedral Fe\textsuperscript{3+} ions in γ-Fe\textsubscript{2}O\textsubscript{3} cause the increase in the first peak intensity of the main band at about 2.7 eV.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig9}
\caption{XPS Fe 2p core-level spectra of various iron deficient Fe\textsubscript{1−δ}O\textsubscript{4} films between γ-Fe\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{3}O\textsubscript{4} on MgO\textsubscript{100} as a function of the NO\textsubscript{2} pressure during deposition.}
\end{figure}

B. Fe\textsubscript{1−δ}O\textsubscript{4} films

Fe\textsubscript{2}O\textsubscript{4} is a mixed-valence compound with a conventional notation of [Fe\textsuperscript{3+}\textsubscript{10}Fe\textsuperscript{2+}\textsubscript{10}Fe\textsuperscript{3+}\textsubscript{10}O\textsubscript{4}. At room temperature, the octahedral Fe\textsuperscript{3+} and Fe\textsuperscript{2+} ions can formally be written as Fe\textsuperscript{2.5+} because of a rapid electron hopping with a frequency of about 10\textsuperscript{-11} sec.\textsuperscript{36} Therefore, the room-temperature Mössbauer spectrum of Fe\textsubscript{2}O\textsubscript{4} consists of only two superimposed sextets, assigned to the tetrahedral Fe\textsuperscript{3+} ions and the octahedral Fe\textsuperscript{2.5+} ions, respectively, as shown in Fig. 1(a). However, the core-hole lifetime in the photoemission process is on the order of 10\textsuperscript{-15} sec,\textsuperscript{37} which is much faster than the hopping frequency. Therefore, the Fe\textsuperscript{3+} and Fe\textsuperscript{2+} ions in octahedral sites are distinguishable by XPS in contrast to Mössbauer spectroscopy.

Figure 9 shows a series of XPS Fe 2p core-level spectra of nonstoichiometric Fe\textsubscript{3−δ}O\textsubscript{4} films between Fe\textsubscript{3}O\textsubscript{4} and γ-Fe\textsubscript{2}O\textsubscript{3} as a function of the NO\textsubscript{2} pressure during growth. The film with δ=0.013 prepared at an NO\textsubscript{2} pressure of 0.166 Pa is nearly stoichiometric Fe\textsubscript{3}O\textsubscript{4}, while the one with δ=0.333 at 1.33 Pa is stoichiometric γ-Fe\textsubscript{2}O\textsubscript{3}. The intensity of the main-peak shoulder at around 709 eV, which is characteristic for the formation of Fe\textsuperscript{2+} ions,\textsuperscript{1−3} increases with decreasing δ. But, in spite of the formation of Fe\textsuperscript{2+} ions, the binding energy of the Fe 2p\textsubscript{3/2} main peak maximum in Fe\textsubscript{1−δ}O\textsubscript{4} hardly seems to depend on δ. On the other hand, the 2p\textsubscript{1/2} main peak gradually shifts to lower binding energy with decreasing δ. In the XPS spectrum of Fe\textsubscript{2}O\textsubscript{3}, the 2p\textsubscript{3/2} satellite at about 719 eV characteristic of the Fe\textsuperscript{3+} ions in γ-Fe\textsubscript{2}O\textsubscript{3} becomes less resolved due to rising intensities at about 716 eV. These latter intensities are normally assigned to the satellite for the Fe\textsuperscript{3+} ions, analogous to the spectrum of wustite, FeO.\textsuperscript{1−3} However, the Fe-O interatomic distance of the octahedral sites in bulk Fe\textsubscript{2}O\textsubscript{3} is about 2% smaller than that in bulk FeO.\textsuperscript{32} The change in the Fe-O distance should influence the p-d hybridization parameters, as discussed above. To reproduce the XPS Fe 2p core-level spectrum for Fe\textsubscript{2}O\textsubscript{3} by a cluster calculation, we tried to optimize these parameters for Fe\textsubscript{3}O\textsubscript{4}. The simulation involved three iron-oxygen clusters, i.e., octahedral Fe\textsuperscript{2+}, octahedral Fe\textsuperscript{3+}, and tetrahedral Fe\textsuperscript{3+} ones.

The simulated XPS Fe 2p core-level spectrum of Fe\textsubscript{2}O\textsubscript{4}, obtained by summation of three spectra of the above clusters, is shown in Fig. 10. The relative binding energies of the Fe\textsuperscript{2+} and the Fe\textsuperscript{3+} spectra were simply determined by subtracting the observed XPS spectrum of γ-Fe\textsubscript{2}O\textsubscript{3} from that of Fe\textsubscript{3}O\textsubscript{4}. The Fe 2p\textsubscript{3/2} main peak maximum of the Fe\textsuperscript{2+} component has a binding energy of 708.5 eV, while that of the Fe\textsuperscript{3+} components in γ-Fe\textsubscript{2}O\textsubscript{3} is 710.6 eV. To optimize the parameter values of Fe\textsubscript{2}O\textsubscript{3}, we referred to the structural parameters of bulk crystals. The Fe-O interatomic distance of octahedral sites in Fe\textsubscript{2}O\textsubscript{4} is enlarged by about 2% compared to γ-Fe\textsubscript{2}O\textsubscript{3},\textsuperscript{32} which should effect the p-d hybridization parameters. For instance, the Harrison’s relations makes T vary with the interatomic distance as d\textsuperscript{−3.5}.\textsuperscript{29} Furthermore, the intra-atomic Coulomb interactions Q and U are screened mainly due to the polarizability of O\textsuperscript{2−}, which increases with

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig10}
\caption{Observed (a) and simulated (b) XPS Fe 2p core-level spectra of a Fe\textsubscript{2}O\textsubscript{4}(100) film on MgO(100). The simulated spectrum labeled ‘‘Total’’ is obtained by a summation of the octahedral Fe\textsuperscript{2+} and Fe\textsuperscript{3+} and the tetrahedral Fe\textsuperscript{3+} components. The parameter values used for the simulation are listed in Table II.}
\end{figure}
decreasing an interatomic distance as $r^{-3}$. The parameters of the Fe$^{2+}$ ions are expected to have an increase in $\Delta$ and $T$, and a decrease in $Q$ and $U$ compared to those of the Fe$^{3+}$ ions because of the increasing electron densities. On the other hand, the interatomic distance of tetrahedral sites of Fe$_3$O$_4$ is slightly decreased in spite of the large increase in unit-cell volume, compared to $\gamma$-Fe$_2$O$_3$. Thus, the spectrum of the tetrahedral Fe$^{3+}$ in Fe$_3$O$_4$ was simulated by using the same hybridization parameters in $\gamma$-Fe$_2$O$_3$.

Following the above procedure qualitatively, the simulated spectrum for Fe$_3$O$_4$ can well reproduce the smeared-out satellite structures between 714 and 720 eV. The broad intensities at about 716 eV can mainly be assigned to the satellite structures of the octahedral Fe$^{2+}$ ions. The satellites in the octahedral Fe$^{3+}$ spectrum also shift their intensities to lower binding energies, but those due to the tetrahedral ions are unchanged. Thus, the unresolved net satellite structures are produced. Unfortunately, our simulation could not reproduce the asymmetric broadening of the Fe 2p main peaks very well. This probably results from the larger bandwidth of the XPS final states for Fe$_3$O$_4$, reflecting the higher conductivity of this material. According to the ZSA diagram shown in Fig. 5, the Fe$^{2+}$ ions in Fe$_3$O$_4$ are plotted in the intermediate regime between the Mott-Hubbard and charge-transfer insulators, just like FeO. However, the higher conductivity in Fe$_3$O$_4$, due to the rapid electron hopping, makes the ZSA classification not applicable to this oxide.

Shown in Fig. 11 are the observed XPS spectra of the valence-band region of the Fe$_{3-x}$O$_x$ films as a function of the NO$_2$ pressure during deposition.

![FIG. 11. XPS spectra of the valence-band region of iron deficient Fe$_{3-x}$O$_x$ films between $\gamma$-Fe$_2$O$_3$ and Fe$_3$O$_4$ on MgO(100) as a function of the NO$_2$ pressure during deposition.](image1.png)

Gradually shifts its position to lower binding energy with increasing Fe$^{2+}$ content. The Fe$^{2+}$ derived spectrum obtained by subtracting the spectrum of $\gamma$-Fe$_2$O$_3$ from that of Fe$_3$O$_4$ has a main band with a shallow binding-energy level at about 0.83 eV. This intensity near $E_F$ can be related with the conducting nature of the Fe$_{3-x}$O$_x$ films. The simulated XPS Fe 3d spectrum shown in Fig. 12(b) was simply obtained by a summation of three spectra of the octahedral Fe$^{2+}$ and Fe$^{3+}$ and the tetrahedral Fe$^{3+}$ ions, similarly to simulate the XPS Fe 2p core-level spectrum. The same parameter values of $\Delta$, $T$, and $U$ derived from the XPS Fe 2p spectra were used for the calculation. Although the observed valence-band spectrum is contaminated by unhybridized O 2p levels, the simulated spectrum can well reproduce the changes in the structures of the satellite band and the main band with shallow binding energy, going from $\gamma$-Fe$_2$O$_3$ to Fe$_3$O$_4$.

![FIG. 12. Observed (a) and simulated (b) XPS spectra of the valence-band region of a Fe$_3$O$_4$(100) film on MgO(100). The parameter values measured in the XPS Fe 2p spectrum (Fig. 10) are used for the simulation. The simulated spectrum labeled ‘‘Total’’ is obtained by the summation of the octahedral Fe$^{2+}$ and Fe$^{3+}$ and the tetrahedral Fe$^{3+}$ components.](image2.png)

V. CONCLUSION

We reported on a systematic analysis of XPS Fe 2p core-level and valence-band spectra of various iron oxide films prepared by NO$_2$-assisted MBE. The observed XPS spectra, which were in good agreement with spectra of bulk crystals, were interpreted using cluster-model calculations. The satellite structures in the XPS spectra were caused by the Fe 3d-O 2p hybridization. The XPS Fe 2p spectrum of $\gamma$-Fe$_2$O$_3$ had a smaller satellite intensity compared to $\alpha$-Fe$_2$O$_3$, because of the larger Fe 3d to O 2p hybridization in $\gamma$-Fe$_2$O$_3$. Furthermore, the XPS valence-band spectrum of $\gamma$-Fe$_2$O$_3$, which was comprised of both Fe 3d and O 2p levels, had a larger normalized intensity than that of $\alpha$-Fe$_2$O$_3$. Both findings indicated an increased covalency of the Fe-O bonds in $\gamma$-Fe$_2$O$_3$ compared to $\alpha$-Fe$_2$O$_3$. By adjusting the NO$_2$ pressure during deposition, it was also possible to obtain Fe$_{3-x}$O$_x$ with a precisely controlled stoichiometry.
With the decrease in $\delta$ of the Fe$_3$O$_4$ films from $\gamma$-Fe$_2$O$_3$ to Fe$_3$O$_4$, the XPS spectra showed gradual changes in their structure, mainly because of the formation of Fe$^{2+}$ ions and an increase in the Fe-O interatomic distance of only the octahedral sites but not of the tetrahedral sites. The smeared-out satellite structure of Fe$_3$O$_4$ could be reproduced by a summation of three different satellite structures derived from octahedral Fe$^{3+}$, octahedral Fe$^{2+}$, and tetrahedral Fe$^{3+}$ ions.

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