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# Preface

Japan Society of Applied Physics (JSAP) celebrated its 80th anniversary in 2012. It decided to accelerate internationalization through globalization. A primary method was to increase the number of participants from overseas countries in the annual academic meetings. In cooperation with the Materials Research Society (MRS), JSAP held MRS-JSAP Joint Symposia during April 9–13, 2012 in San Francisco. One of 12 symposia, "Nanocomposites, Nanostructures and Heterostructures of Correlated Oxide Systems", was organized by Tamio Endo (Mie University), Nobuyuki Iwata (Nihon University), Hiroaki Nishikawa (Kindai University), Anand Bhattacharya (Argonne National Laboratory) and Lane W. Martin (University of Illinois). In the beginning Kazuhiro Endo (Kanazawa Institute of Technology) contributed to the growth of the symposium. This symposium was quite successful, with 180 presenters, 43 submissions of papers for MRS proceedings, and 17 submissions for the Japanese Journal of Applied Physics' special issue. These numbers were the highest among the 12 kindred symposia.

Future electronics will increasingly rely on oxide materials because of their unique functions. With advances in the synthesis and characterization of oxide thin films and nanostructures has come the observation of exciting new materials phenomena. The parallel fields of oxide heteroepitaxy and nanomaterials both exploit surfaces, interfaces, and boundaries in materials to achieve better performance and new properties. Core to both fields is the ability to control these structures at unprecedented atomic levels. Because of these common themes, we aimed to bring together researchers from both communities to identify and illuminate new areas of interaction and collaboration. The combined expertise of the two fields was explored and connected to major challenges across the disciplines. At their core, the ability to control multi-layered oxide thin film heterostructures to possess well-defined surfaces and interfaces makes them a novel extension and an ideal form of nanocomposite systems. This symposium, in particular, focused on correlated electron phenomena in such nano- and heterostructures.

The topics included were:

- Synthesis and characterization of oxide nanocomposites/nanomaterials, artificial two-dimensional sheets of nanoparticles, heteroepitaxial thin films, and multi-layered systems.
- Characterization and control of defects in oxide nanocomposites and heterostructures (including changes from heterostructure to nanocomposite by heavy radiation damage).
- Theoretical and computational approaches to such materials.
- Studies of functional oxide materials arising from electron correlations (i.e., magnetic, dielectric/ferroelectric, superconducting, etc.).
- Studies of interfacial properties in such materials (i.e., ferromagnetic/superconductor, novel p–n junctions, exchange bias, novel properties at heterointerfaces).
- Magnetization reversal and phase separation in such materials.
- ZnO/Manganites novel p–n junctions, resistive switchings, magnetic field modulations.

The invited speakers were:

Ulrich Habermeier (Max-Planck-Inst.), Kai Liu (Univ. California, Davis), Ivan Bozovic (Brookhaven Nat. Lab.), Hideomi Koinuma (Univ. Tokyo), Jacobo Santamaria (Univ. Complutense), Josep Nogues (Univ. Autonoma de Barcelona), Suzanne te Velthuis (Argonne Nat. Lab.), Akira Ohtomo (Tokyo Inst. Tech.), Judith Driscoll (Univ. Cambridge), Katsuhisa Tanaka (Kyoto Univ.), Sibylle Gemming (Helmholtz-Zentrum Dresden-Rossendorf), Peter Badica (INCDFM), Shigetoshi Ohshima (Yamagata Univ.), Reji Philip (Raman Res. Inst.), Hitoshi Tabata (Univ. Tokyo), Tetsuya Yamamoto (Kochi Univ. Tech.), Toshio Kamiya (Tokyo Inst. Tech.), Lakshmi Reddy (S. V. D. College).

The high level of interest was established by the huge number (180) of papers presented, attendance, and vigorous discussions in this symposium during the four-day sessions. Furthermore the stage was set prior to the symposium by a comprehensive tutorial on "Oxide Heterostructures and Nanostructures—Fabrication, Properties, Magnetic Coupling, and Applications". It was quite friendly and interactive, with keen Q/A, which attracted many scientists from academia, governmental and industrial institutes. The symposium was composed of invited, oral, and poster presentations. In this symposium, we set the special theme, i.e., clarification of relations among nanocomposites, nanostructures, and heterostructures to get a deeper understanding of nanocomposites. Then an international collaborated research was arranged. Its idea is that clear and systematic understanding of nanocomposites is very difficult because they do not have regular structures due to complex grain boundaries (interfaces). Introducing ion-irradiated damage into heterostructures with well-ordered and defined heterointerfaces, gradually randomizes the nanocomposites. We can trace structures and natures during this process, leading to a better understanding of nanocomposites. According to this idea two papers were presented at the symposium by the international group (Sybille Gemming, Julia Osten, Juergen Fassbender, Kai Liu and Peter Greene). They gave interesting results but those are only a starting point. We hope the group receives magnificent results and that their achievements are published in following books.

The consecutive series of JSAP-MRS Joint Symposia was held during September 16–20, 2013 in Kyoto, and we organized a similar symposium of "Synthesis and Magnetic Properties of Oxide Nanocomposites and Heterostructures". It was also very successful. We obtained 89 presenters, 18 submissions of papers for JJAP, and 11 submissions for MRS Proceedings, which were, again, the greatest number. This book is published in memory of those two splendid, consecutive, special symposia. The authors of this book are selected from the two symposia. We are planning to publish the second book where authors will be selected from the rest of the presenters of the two symposia. It should be mentioned that Paolo Mele (Muroran Institute of Technology) contributed a lot to this publication process.

Kinokawa, Japan — Hiroaki Nishikawa
Funabashi, Japan — Nobuyuki Iwata
Tsu, Japan — Tamio Endo
Muroran, Japan — Paolo Mele
June 2016

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# Editors and Contributors

## About the Editors

**Hiroaki Nishikawa** holds Ph.D. (Osaka University) and M.S. (Osaka University) degrees. Currently he is Associate Professor at Kindai University and is Visiting Researcher at University of Twente 2007–2008 (The Netherlands). His research interests include oxide electronics, oxide heterointerfaces and their interface properties, and bioceramic thin films. He has participated in many conferences such as International Conference Organizer of HTCMC 9 in conjunction with GFMAT 2016 (Toronto, Canada), IUMRS-ICAM 2015 (Jeju, Korea), JSAP-MRS Joint Symposia 2013 (Kyoto, Japan), etc. and in many invited talks such as Keynote Speaker of IUMRS-ICEM 2014 (Taipei, Taiwan).

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**Paolo Mele** is currently Associate Professor Lecturer at Research Center for Environmentally Friendly Materials Engineering, Muroran Institute of Technology (Muroran, Hokkaido, Japan). He obtained a Masters degree in Chemistry and Ph.D. in Chemical Sciences at Genova University (Italy). In 2003 he moved to ISTEC-SRL in Tokyo to study melt-textured ceramic superconductors. Then he worked as postdoc at Kyoto University (JSPS fellowship) from 2004 to 2007, at Kyushu Institute of Technology (JST fellowship) from 2007 to 2011 and at Hiroshima University (as lecturer) from 2011 to 2014 before reaching his current position. His research interests include materials for energy and sustainable development (superconductors and thermoelectrics); fabrication and characterization of thin films of oxides, ceramics and metals; study of the effect of nanostructuration on the physical properties; thermal transport; and vortex matter. He is the author of more than 90 papers in international scientific journals and four book chapters, and has two patents and has contributed to hundreds of communications at international conferences. He edited the book "Oxide Thin Films, Multilayers and Nanocomposites" for Springer in 2015.

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# Chapter 1
# Functional Iron Oxides and Their Heterostructures

**Munetoshi Seki and Hitoshi Tabata**

**Abstract** Iron oxides, which are also called ferrites, have been known to humans since ancient times and have been the subject of intensive research activity from fundamental as well as practical perspectives for a long time. One of the most advantageous properties of iron oxides is that they are chemically stable and nontoxic. In addition, Fe and O are earth-abundant elements [high Clarke numbers for Fe (4.7) and O (49.5)]. These features mean that the ferrites are suitable for applications in low cost, environmentally-friendly electronics. In this chapter, we examine some of the functional iron oxides and their heterostructures. First, we focus on the growth of FeO (wüstite) epitaxial thin films, and their properties as *p*-type transparent semiconductors will be discussed. Next, we will consider α-$Fe_2O_3$ (hematite), which is well known as the main component of red rust. It is demonstrated that band engineering and control of the crystal growth direction of α-$Fe_2O_3$ are useful to enhance its photoelectrochemical properties for high efficiency water splitting using sunlight. The third topic is $Fe_3O_4$ (magnetite), which is known to be a ferromagnetic oxide semiconductor. The control of the carrier type in $Fe_3O_4$ and its possible application to spintronic devices will be discussed. Finally, we will focus on the spin-fluctuation system in iron oxides. The long-term potentiation with the photomemory effect is observed in a Si-substituted garnet ferrite with high temperature spin-glass-like properties, which mimics the pre- and post-synaptic potentials of biological systems.

**Keywords** Iron oxides · Magnetite · Hematite · Photoelectrochemical water splitting · Oxide spintronics

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## 1.1 Introduction

The challenge of developing a new material technology that can solve increasingly serious problems on a global scale, pertaining to the environment, energy, and resources, is being pursued actively. It is against such a backdrop that iron oxide, which is an inexhaustible resource that is nontoxic and offers a superior environmental affinity, is drawing much attention. Iron oxide has been used in a various devices, such as recording media to communication equipment. It is a representative magnetic material that has been supporting the development of modern industry from the ground up. The aspects of iron oxide responsible for its wide applicability are its high magnetic transition temperature (500 °C and higher) and superior chemical stability. Most iron oxide materials currently being used in practical applications contain iron in the stable +3 valence state. Their localized spin allows for strong bond formation via oxygen ions (i.e. superexchange interaction) to achieve stable magnetic structure and magnetic field responsiveness, as well as high insulation, all of which are essential for practical applications. Transition metal oxides that contain iron oxide, on the other hand, feature an attractive characteristic of their electrical, magnetic, and optical properties varying significantly according to the valence of metal ions [1, 2]. In iron oxides, the control of the valence states of Fe ions has been particularly difficult, and this has been a significant barrier for the progress of research and development in the application of new functional materials. This chapter describes the attempts made to control the valence of iron oxide using the film growth technique based on pulsed laser deposition (PLD). A variety of iron oxide thin films fabricated using these methods are then explored for their potentials as functional materials.

## 1.2 FeO: Transparent P-Type Oxide Semiconductor

Iron oxides are known to exhibit a wide range of physical properties and crystal structures. For example, multifunctional bismuth ferrite ($BiFeO_3$) has been attracted considerable owing to its numerous promising applications in multiferroic and photovoltaic devices [3, 4]. The triangular antiferromagnet ($RFe_2O_4$; R=Ho–Lu, In) with a multilayered structure, which was discovered in the 1970s [5], exhibits charge-order-type ferroelectricity, and its magnetoelectrical effect is currently the subject of intensive study [6, 7]. Furthermore, much attention has been focused on the giant magneto-optical effects of rare-earth iron garnets ($R_3Fe_5O_{12}$) from the perspective of their practical applications, mainly in the field of optical communications [8–10]. The wide diversity in the physical properties of iron oxides mentioned above is strongly related to the valence state of Fe ions. Therefore, control of the Fe valence in the ferrites is strongly required to promote their further application as functional oxide materials. However, in general, the $Fe^{3+}$ valence state is stable and hence the control of the Fe valence in iron oxides is difficult. The

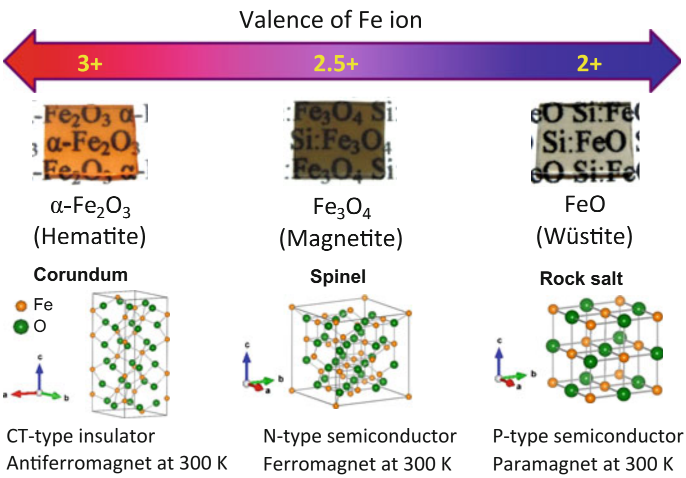


**Fig. 1.1** Basic iron oxides with different valence state of Fe ions in the electron conduction path and their physical properties. Images and crystal structures of these iron oxides are also shown

authors found that the basic crystal phases of iron oxide, namely, α-$Fe_2O_3$ (hematite), $Fe_3O_4$ (magnetite), and FeO (wüstite), can be separately fabricated using the technique of PLD (see Fig. 1.1) [1].

In this section, we focus on FeO thin films with a rock-salt crystal structure. FeO has attracted scientific interest over a long period because of its importance as a possible chemical component of the Earth's core. Furthermore, FeO is currently a subject of intense investigation in a wide variety of research fields such as spintronics and chemical engineering [11–13]. Although its physical properties still remain unclear, it is generally recognized that FeO exhibits *p*-type semiconducting behavior originating from the Fe deficiency. Moreover, theoretical investigations based on band calculations have revealed that its bandgap energy is 2.5–3.0 eV [14–16]. Therefore, FeO can be regarded as a candidate *p*-type wide-gap semiconductor; such semiconductors are of great importance for novel applications such as blue and ultraviolet (UV) light-emitting diodes (LEDs), and UV sensors. Furthermore, the simple crystal structure of FeO is favorable from the viewpoint of constructing a rich variety of heterostructure devices based on an oxide p-n junction. However, FeO is thermodynamically unstable [17, 18], and pure FeO has only been observed as a nanofilm or as nanometer-size islands [19, 20]. Accordingly, little has been reported on the epitaxial growth of FeO thin films. These problems are severe barriers not only to further understanding its basic properties, but also to its use in practical applications. The instability of FeO is related to its tendency to decompose into spinel type $Fe_3O_4$ and metal Fe below 575 °C. Moreover, FeO is easily oxidized to higher valence oxides such as $Fe_3O_4$ and α-$Fe_2O_3$. To reduce this instability, Si substitution is useful. It is well known that the spinel Si:$Fe_3O_4$ system with a high Si content is only stable at high temperatures (~1200 °C) and pressures (6–10 GPa) [21]. Therefore, the extraction of the spinel phase may be suppressed