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Studies of low-temperature growth of ferromagnetic iron oxide thin films for spin-dependent devices

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Abstract

This dissertation describes low-temperature growth of ferromagnetic iron oxide thin films with high quality required for applications to spin-dependent devices. The objectives of the dissertation are to establish a technique for low-temperature growth of ferromagnetic iron oxide thin films with high quality and to demonstrate that the obtained thin films are promising for advanced applications such as spin-dependent devices.

In this dissertation, first, the current status in research on magnetoresistance effects in spin-dependent devices such as spin-tunneling devices and spin-valve devices using ferromagnetic metals, and advantages of their devices using ferromagnetic iron oxides with half-metallic properties were described. The basic knowledge for ferromagnetic iron oxides (spinel ferrites) and film-growth technologies were outlined. It was indicated that these applications require controlled low-temperature growth of the ferromagnetic iron oxide films with high quality.

In the chapter 2, criteria for the film growth which is a key factor to achieve low-temperature growth of oxide thin films with high quality were described. The author pointed out that kinetic energy of particles travelling on the film surface is significant factor dominating the low-temperature growth of the thin films, and selected a pulsed laser deposition (PLD) in high vacuum and a metalorganic chemical vapor deposition (MOCVD) as deposition technique. The techniques used for deposition of the films and for structural as well as magnetic characterization were described in chapter 3.

In the studies described in chapter 4 to 7, structural and magnetic properties of spinel ferrite thin films prepared by these methods selected by the criteria were given.

In the chapter 4, the preparation of Fe_3O_4 thin films by plasma assisted MOCVD was described in detail. The Fe_3O_4 films were grown Si substrate by plasma assisted MOCVD using acetylacetonate iron complex as a gas source. Part of the source molecules were decomposed into the iron oxide molecules and the intermediate by plasma applied in a diffusion process to the substrate surface. These reaction species allowed growth of Fe_3O_4 films with low carbon contamination and good surface morphology at low temperature of 400 °C. However, the growth of Fe_3O_4 films with higher quality at lower temperatures was demanded for applications.

In chapter 5 to 7, structural and magnetic properties of spinel ferrite thin films prepared by PLD were investigated as a function of several growth parameters such as temperature and oxygen pressure etc. Significant factors dominating the growth of the films with high quality were determined from the study. Chapters 5 and 6 described conditions of low-temperature growth for MFe_2O_4 (M = Ni, Fe, (Mn, Zn), (Ni, Zn)) thin films, and the growth conditions for obtaining spinel ferrite epitaxial films with high quality. The MFe_2O_4 (M = Ni, Fe, Co, (Mn, Zn), (Ni, Zn)) thin films were grown on (0001)-basal sapphire substrates. In particular, the author has successfully achieved the epitaxial growth of (111)-oriented (M, Zn)Fe_2O_4 films (M = Ni, Mn) with high crystalline quality and good surface smoothness on the sapphire substrates at room temperature for the first time. When deposited at oxygen pressures of 1.0×10^{-4} Torr to 1.0×10^{-6} Torr, the films crystallized in spinel-type crystal structure at room temperature. On the other hand, when deposited at high oxygen pressure of 1.0×10^{-2} Torr, the films crystallized in spinel-type structure at high substrate temperatures of more than 100 °C. Such a low-temperature growth of the ferrite films was ascribed to high kinetic energy of the ablated particles at low oxygen pressures and to the low deposition rate which permits the sufficient oxygenation of the ablated particles. The films obtained at the high oxygen pressures had poorer crystalline quality than that at low oxygen pressures. These results indicate the high potential of PLD in high vacuum for obtaining high quality spinel ferrite films at low temperatures. In the chapter 7, the surface morphology of Mn-Zn ferrite thin films grown on sapphire substrates and with the α-Fe_2O_3 underlying layers was described, and the effect of the modified surface on the film growth was discussed. The Mn-Zn ferrite thin films were deposited on sapphire substrates and with epitaxial thin layers of α-Fe_2O_3. The films (about 50 nm thick) on a α-Fe_2O_3 layers (thickness: $t \leq 50$ nm) had a surface with the average roughness of less than 0.4 nm, smaller than that (1.1 nm) on sapphire substrate. Especially, the author has successfully achieved the epitaxial growth of (111)-oriented (Mn, Zn)Fe_2O_4 films with a smooth surface on an atomic scale (average roughness: 0.1 nm) on sapphire substrates with epitaxial thin layers of α-Fe_2O_3 for the first time. Such an effect of the modified surface on the film by introducing underlying layer (α-Fe_2O_3) was primarily ascribed to the good lattice matching between the (111)-oriented Mn-Zn ferrite film and the (0001)-oriented α-Fe_2O_3 layer. It was revealed that layer modifying a large lattice mismatch between the film and substrate is required for achieving the growth of the film with a good smooth surface. From the results obtained in chapter 4 to 7, it was suggested that the PLD in high vacuum allows the low-temperature growth of ferromagnetic iron oxide thin films being suitable for applications to spin-dependent devices.

Next, using the PLD in high vacuum, trilayer structures in which the spinel ferrite layers are separated by a thin nonmagnetic layer were fabricated practically. In chapter 8 to 10, the experimental results and discussion for the junctions were described.

In the chapter 8, the magnetoresistance of the trilayer structures in which conductive ferrite layers of Mn-Zn ferrite and Co ferrite are separated by a thin nonmagnetic conductive layer of In_2O_3 was reported. The trilayer structures were fabricated practically on (0001) sapphire substrates by PLD in high vacuum. The magnetoresistance (MR) change in the junction was observed about 0.3 % at maximum. From the results of magnetic measurements, it was suggested that the observed change in the junction may be attributed to the intrinsic property of the junction based on the half-metallicity of the spinel ferrite. However, the observed MR change is much smaller than that expected from the half-metallicity of the ferrite. Possible reasons the small magnetoresistance were discussed. It was suggested that investigations of interface magnetism in the junction are required.

In the chapters 9 and 10, growth conditions of the spinel ferrite layer and the nonmagnetic thin layer required for obtaining a good tunnel characteristics were investigated. In the chapter 9, the optimum growth condition of stoichiometric Fe_3O_4 thin film which is one of the promising ferromagnetic layers for spin tunneling devices was reported. Further the stability of Fe_3O_4 thin films for thermal oxidization was described. The epitaxial thin films of $Fe_{3-\delta}O_4$ were prepared on (100) MgO substrates. These films had smooth surfaces on an atomic scale along with extremely high crystalline quality. It was found from the resistivity and XPS measurements that thin films of nearly stoichiometric Fe_3O_4 are obtained at 300 °C in oxygen pressure of 1.0×10^{-6} Torr and the conditions for growing the stoichiometric Fe_3O_4 thin film lie in a narrow range. In addition, it was indicated that low temperature deposition below 200 °C is required for the insulating oxide layer onto the Fe_3O_4 layer in the fabrication process of the tunneling junctions even at oxygen pressure as small as 1.0×10^{-5} Torr. The chapter 10 described the electrical properties of MgO epitaxial thin film which is a promising insulating layer for spin tunneling devices using Fe_3O_4. It was found that the epitaxial thin films of MgO with high crystalline quality are successfully grown at a limited condition of temperature ($\leq$ 200 °C) and oxygen pressure ($\leq 1.0 \times 10^{-5}$ Torr) at which no degradation of the Fe_3O_4 underlying layer occurs. The Au/MgO/Fe_3O_4 junctions with the MgO film prepared at the limited condition showed the nonlinear current-voltage curves being characteristic of the electron tunneling. The barrier height and thickness were estimated at 0.9 eV and 2.5 nm, respectively, by fitting the current-voltage curve of the junction using the MgO layer with 3 nm thickness to Simmons' formula. The values were in consistent with those estimated by taking the reduction of barrier height due to image force into account. It was demonstrated by these results that the MgO insulating layer with high electrical quality for spin tunneling devices can be grown on Fe_3O_4 underlying layers without its degradation, the oxidization of the Fe_3O_4 surface. From the results obtained in chapter 8 to 10, it was suggested that it enables to fabricate the junctions using ferromagnetic iron oxides with high quality.

In the chapter 11, the conclusion obtained through this study on low-temperature epitaxial growth of spinel ferrite thin films were described. Finally, the author should note that it is possible to grow ferromagnetic iron oxide thin films at low temperatures being suitable for spin-dependent devices by the PLD in high vacuum, and lead to applications for the devices.

Keywords: Low-temperature epitaxial growth, Pulsed laser deposition, Metalorganic chemical vapor deposition, Ferromagnetic iron oxides, Spin tunneling junction, Half-metallic materials