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Evaluation of the electronic states in highly Ce doped Si films grown by low temperature molecular beam epitaxy system

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A B S T R A C T

Highly Ce doped single crystalline Si films with high crystallinity, smooth surface and uniformly distributed Ce were deposited by low-temperature grown molecular beam epitaxy (LT-MBE) system. The lattice parameter increases with increasing Ce concentration below 0.2 at%, suggesting that the formation of substitutionally dissolved Ce increases. The donor level of Si homoepitaxial film without Ce doping is calculated as 57 meV originated in the formation of dangling bonds probably due to low temperature growth. Although all films show n-type conduction, electron density decreases with increasing the Ce concentration below 0.5 at%, suggesting Ce^{3+} ion at substitutional site in Si acts as an acceptor. However, the conduction type does not change from n-type to p-type, indicating that the density of the Ce^{3+} ion is not enough to change the conduction type. *J*–*V* characteristics at the measurement temperature from 180 to 300 K were evaluated by using metal–insulator–semiconductor (MIS) structure. The generation energy of electron–hole pair is calculated by Arrhenius plot of resistance at depletion layer. The charged state at the mid gap in Si is formed by Ce doping.

1. Introduction

Rare earth (RE) doped semiconductors have been paid much attention because they show unique optical and magnetic characteristics. As matrixes, GaAs [1–3], GaN [4–9], AlGaAs [10], Si [1,11–16,22–32], and SiO_2 [17–21] have been reported. Er [1–3,10–21], Eu [4,5,9], Gd [6–8], Yb [10] and Ce [22–32] have been studied as rare earth dopants. For example, Er doped materials have been attracted enormous interest due to the emission at the photon energy of 1.54 μm originated in an intra 4*f* shell transition between the $^4I_{12/2}$ and the $^4I_{15/2}$ levels [13], that is attractive for silica optical fibers and optical amplifier [16]. On the other hand, Gd doped GaN shows ferromagnetic with high Curie temperature above 400 K [8]. The detection of an induced magnetic moment of Eu^{3+} ions in GaN which is associated with the $^7F_2$ final state of $^5D_0$ to $^7F_2$ optical transitions emitting at 622 nm has also been reported [9].

We have been interested in RE doped single crystalline Si films. Ce, which has one 4*f* electron, is one of the most interesting RE elements because Ce-based compounds show attractive phenomena originated in valence fluctuation [33–35]. Therefore, we have studied the magnetic and magneto-transport properties of Ce doped Si (Si:Ce) epitaxial films using solid source molecular beam epitaxy system (MBE) that show very interesting phenomena such as ferromagnetic ordering [26,27], spin-glass-like behavior and giant magneto-resistance effect [25,31]. Although most of them were observed in the p-type Si:Ce, we have not elucidated if the phenomena are originated from spin–hole interaction, because the films slightly include silicides. Low temperature growth enables to obtain Si:Ce films with high concentration and uniform distribution of Ce without including precipitation of a second phase such as Ce silicides [24–28,30–32]. However, these films show n-type conduction with high carrier concentration and paramagnetic behavior [30,32]. To discuss the origin of above mentioned ferromagnetic related interesting phenomena, we have to investigate the solid solubility of the Ce and the electronic state in Si epitaxial films because the magnetic and electronic properties of magnetic impurity doped semiconductors depends on the distribution and local environment of the dopant [36]. In this paper, change in the carrier density, formation energies of electron and hole, and the lattice constant against the Ce concentration were evaluated and the solid solubility state and the electronic states of Ce for low temperature grown Si:Ce epitaxial films with the Ce concentration below 1.0 at% are discussed.

2. Experiment

Si:Ce epitaxial thin films were deposited on (001) Si or Si on insulator (SOI) substrates by a solid source MBE method at a base

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pressure in the order of 10^{-10} Torr. The substrate was chemically cleaned with Semico Clean 23 (Furuuchi Chemical). After immersion in 1.0% HF solution for 2 min, the substrate was inserted into an ultra-vacuum MBE chamber. The substrate was carefully outgassed at 600 °C and β-SiC was intentionally formed at 830 °C to fix carbon at the surface. After the growth of the 30-nm-thick Si buffer layer, the sample was annealed at 750 °C in order to form a step and terrace surface structure with the double domained reconstructed surface structure of 2×1 and 1×2 observed by Reflection High Energy Electron Diffraction (RHEED). An 100-nm-thick Si:Ce layer was grown by simultaneously evaporated on the Si buffer layer at 600 °C by using Knudsen cells (k-cell) of Si and Ce. A 5-nm-thick Si capping layer was finally deposited at the same temperature after the Si:Ce deposition. The deposition rate evaluated by RHEED oscillation is fixed as 40 nm/h. The Ce concentration was varied from 0.1 to 1.0 at% evaluated by electron prove micro analyzer calibrated with Rutherford backscattering and secondary ion mass spectroscopy. The substrate and k-cell temperature was measured with a thermocouple and a pyrometer. The surface morphology and structure were analyzed by in-situ RHEED operated at the incident electron energy of 30 keV. The crystal structural analysis was also performed by ex-situ x-ray diffraction (XRD). For the electrical measurement, the Al electrode was deposited on the samples through a shadow mask after removal of native oxide at the surface. The electrical resistivity and the Hall Effect were performed in the van der Pauw configuration at the temperature from 70 to 300 K. In order to evaluate the electron states of Si:Ce films, the metal insulator semiconductor (MIS) capacitor structure was fabricated. Around 10-nm-thick Si oxy-nitride was prepared by Atmospheric Pressure Plasma Enhanced Chemical Vapor Deposition (APE-CVD) system [37,38]. The capacitance–voltage (C–V) and current–voltage (J–V) characteristics were also evaluated by using a LCR meter (HP4284A) and a pico-ampere meter (4140B) at the measurement temperature from 180 to 300 K.

3. Results and discussion

Fig. 1 shows the in-situ RHEED images of Si:Ce films grown at 600 °C. All films show a 2×1 reconstructed surface throughout the growth without the Ce concentration above 1.0 at%. And the root mean square of these samples measured by Atomic Force Microscopy is below 0.5 nm. Although the streak pattern diffraction gradually changes to spotty pattern suggesting the three dimensional growth under the Ce concentration of 1.0 at%, the RHEED image of Si:1.0 at% Ce shows sharp streaky pattern with 3-folded structure. Although this reconstructed surface structure appears in highly Ce doping Si films, the surface becomes smooth [32] probably due to the relaxation of stress induced by incorporation of Ce with very large ionic radius.

The 004 diffraction peak of XRD for Si:Ce films has interference fringes indicating that the films have very smooth surface. However, the strong peak of substrate prevents from calculation of the lattice constant of the films normal to the surface. In order to deconvolute the diffraction of the film from that of the substrate, the lattice spacing of (113) (d_{113}) is evaluated. Fig. 2(a) shows the change in the d_{311} as a function of Ce concentration. The d_{311} of the Si homoepitaxial film without Ce is smaller than that of Si single crystal probably originated from the formation of defect formation such as Si vacancy. The d_{311} increases with increasing the Ce concentration below the 0.2 at% suggesting that the formation of Ce^{3+} ion in substitutional site of Si because the covalent radius of Ce^{3+} ion is larger than that of Si. However, it decreases with increasing Ce concentration between 0.3 and 0.6 at%, suggesting that the defects such as Si vacancy or Ce related defects, which make the lattice constant small, increase. The formation of these defect and the solid solubility state of Ce change the carrier concentration in films. Fig. 2(b) shows the change in the carrier concentration as a function of Ce concentration. The Si homoepitaxial film without doping Ce shows n-type conduction with the carrier density 5×10^{16} cm^{-3}. Because the donor level of this film is calculated as 57 meV by Arrhenius plot of carrier density, this n-type conduction is originated in the formation of dangling bonds due to low temperature growth of Si. With increasing Ce concentration, carrier density decreases below the Ce concentration of 0.3 at%, indicating that the electrons are compensated by the holes generated by substitutionally dissolved Ce^{3+} ions. This tendency is similar to the increase of d_{113}. However, the conduction type does not change from n-type to p-type, indicating that the density of the Ce^{3+} ion in substitutional site of Si is not enough to change the conduction type. It is also considered that the lattice strain due to the Ce^{3+} ion, which has large covalent radius, forms the Si vacancy. So there are many electrons and holes in Si:Ce films. Although the Hall Effect measurement was done at low temperature from 70 to 300 K, high resistivity of the film below 250 K prevents from evaluating the Hall voltage at low temperature.

In order to discuss the electronic state of Si:Ce thin films, MIS structure has been fabricated. As the insulator layer, ultra-thin SiON layer with the thickness of less than 10 nm was formed using atmospheric pressure (AP) plasma. AP plasma oxynitridation enables to low temperature fabrication of highly resistive dielectric ultra-thin films. Hayakawa et al. have reported that the nitridation thickness of Si saturates at 2 nm (self-limitation), which is independent on the substrate temperature [39]. Pure nitrogen gas (99.999%) of 10/min

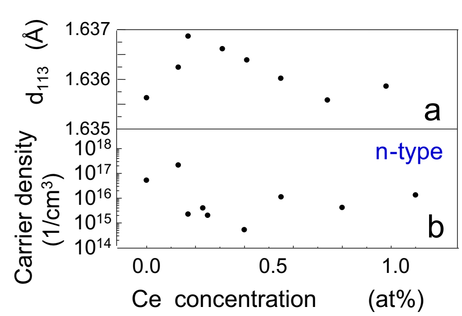

Fig. 2. Change in the lattice parameter of (113) (d_{113}) (a) and carrier density (b) as a function of the Ce concentration. All samples show n-type conduction.

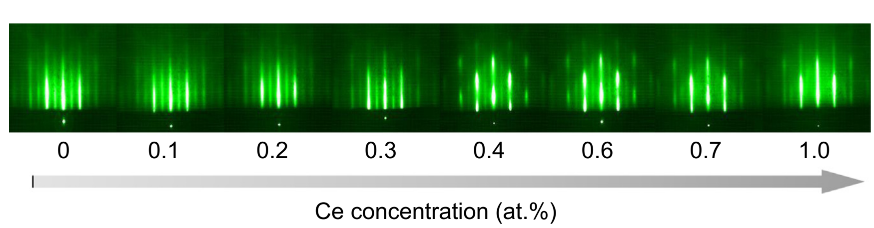

Fig. 1. Change in the RHEED images of Si:Ce films grown at 600 °C with increasing Ce concentration. Incident direction of the electron beam was parallel to [110] direction. The film thickness is 100 nm.

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