

# Ferromagnetism in Ge and Chalcopyrite Semiconductors

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## 1. 서론

The injection of spins into nonmagnetic semiconductors has recently attracted great interest due to the potential to create new classes of spin-dependent electronic devices. A recent strategy to achieve control over the spin degree of freedom is based on dilute ferromagnetic semiconductors. Ferromagnetism has been reported in various semiconductor groups including II-VI, III-V, IV, and II-IV-V<sub>2</sub>. Firstly, I will present some interesting magnetic and transport properties in transition metal (V, Cr, Mn, Fe, Co, Ni, Cu)-doped Ge single crystals. We also introduce new pure ferromagnetic semiconductors, MnGeP<sub>2</sub> and MnGeAs<sub>2</sub>, exhibiting ferromagnetism and a magnetic moment per Mn at 5K larger than 2.40 B.

## 2. 실험 방법

For the preparation of single-crystalline Ge<sub>1-x</sub>Mn<sub>x</sub>, we used high-purity (99.999%) germanium (Ge) and manganese (Mn) powders as starting materials with a particle size of < 200 mesh to maximize the surface area and thereby enhance the reaction kinetics. First, the powders were weighed and loaded into thick-walled quartz ampoules. Then the ampoules were evacuated (< 10<sup>-6</sup> Torr) and sealed. After encapsulation, the sealed ampoule was mixed, loaded into a vertical furnace, and heated slowly to form single-phase (Ge<sub>1-x</sub>Mn<sub>x</sub>). For single crystal growth, the temperature was slowly cooled at 0.5 °C/h to a point below the melting temperature (933 °C for Ge) and thereafter at 100 °C/h. We have prepared 8 mm × 8 mm single crystals with x = 0, 0.0044, 0.013, 0.038 and 0.062. For single crystal MnGeP<sub>2</sub> preparation, the heating cycle was 50 °C/h to 530 °C, 24-h soak, 4°C/h to 630°C, 24-h soak, 20 °C/h to 1130 °C, 168 h soak. The reason for maintaining the intermediate temperatures is to avoid excessive pressure buildup due to the high vapor pressures of P, and possible explosion by forming MnP. We have prepared 3 mm × 3 mm single crystals by slowly cooling at 0.5 °C/h between 1130 and 900 °C, and thereafter at 100 °C/h.

## 3. 실험 결과 및 고찰

We have successfully fabricated highly Mn-doped (up to 6%) Ge single crystals. Alloys with lower Mn concentrations showed paramagnetism due to localized magnetic ions. Ge<sub>0.94</sub>Mn<sub>0.06</sub> showed ferromagnetic ordering at 285 K, as determined from temperature dependent magnetization and resistance measurements. The coercive field was 1260 Oe at 250 K. Slightly transition metal(V, Cr, Mn, Fe, Co, Ni, Cu)-doped Ge single crystals showed huge resistance increases about 10<sup>6</sup> times at low temperature, which might be used as a resistance temperature sensor. New pure ferromagnetic semiconductors, MnGeP<sub>2</sub> and MnGeAs<sub>2</sub>, exhibit ferromagnetism and a magnetic moment per Mn at 5K larger than 2.40 B. The calculated electronic structures using the FLAPW method show an indirect energy gap of 0.24 and 0.06 eV, respectively. We have observed spin injection in MnGeP<sub>2</sub> and MnGeAs<sub>2</sub> magnetic tunnel junctions through semiconducting barriers.

#### 4. 결론

It is plausible that magnetically doped Ge and Si and related materials can open the way to room temperature spintronic devices. Newly-synthesized  $\text{MnGeP}_2$ ,  $\text{MnGeAs}_2$ ,  $\text{MnSnP}_2$ , and  $\text{MnSnAs}_2$  have the chalcopyrite crystal structure.  $\text{MnSn(P,As)}_2$  are metals and  $\text{MnGe(P,As)}_2$  are semiconductors with energy gaps of 0.24 and 0.06 eV. We have observed spin polarization of the carriers and spin injection in a magnetic tunnel junction. The results of the present investigation suggest that chalcopyrite  $\text{Mn(Ge,Sn)(P,As)}_2$  and related materials are serious contenders for room temperature spintronic devices.