

## NOVEL SPINTRONIC MATERIALS BASED ON FERROMAGNETIC SEMICONDUCTOR CHALCOPYRITES

G. A. MEDVEDKIN and S. I. GOLOSHCHAPOV

*Ioffe Physico-Technical Institute, Russian Academy of Sciences  
Polytechnicheskaya Street 26  
Sankt-Petersburg 194021, Russia*

V. G. VOEVODIN

*Siberian Physico-Technical Institute  
Tomsk State University, Novosobornaya Square, 1  
Tomsk 634050, Russia*

K. SATO and T. ISHIBASHI

*Department of Applied Physics  
Tokyo University of Agriculture and Technology, Koganei  
Tokyo 184-8588, Japan*

S. MITANI and K. TAKANASHI

*Institute for Materials Research, Tohoku University, Sendai  
Sendai 980-8577, Japan*

A. FUJIMORI, Y. ISHIDA and J. OKABAYASHI

*Department of Physics, University of Tokyo, Bunkyo-ku  
Tokyo 113-0033, Japan*

D. D. SARMA

*Solid State and Structural Chemistry Unit, Indian Institute of Science  
Bangalore 560012, India*

H. AKAI and T. KAMATANI

*Department of Physics, Osaka University, Toyonaka  
Osaka 560-0043, Japan*

Ternary diamond-like compounds in II–IV–V<sub>2</sub> semiconductor system heavily-doped with transition *d*-element Mn have been recently prepared. The materials grown in both forms — single crystal layers and polycrystalline bulks — exhibit well defined ferromagnetic hysteresis with a saturation behavior in the magnetization curve up to above room temperature. Curie temperatures are of  $T_C = 310$  K to 320 K for  $(\text{Cd}_{1-x}\text{Mn}_x)\text{GeP}_2$  and  $(\text{Zn}_{1-x}\text{Mn}_x)\text{GeP}_2$  compounds. The chemical states in the bulk of  $\text{ZnGeP}_2:\text{Mn}$  and interface of Mn-doped ferromagnetic layer on  $\text{ZnGeP}_2$  (001) crystal, have been clarified by electron paramagnetic resonance and *in situ* photoemission spectroscopy. The

as-prepared surface consists of Ge-rich, metallic Mn-compound. In and below the sub-surface region, dilute  $\text{Mn}^{2+}$  species as precursors of the DMS phase exist.  $\text{Mn}^{2+}$  ions are paramagnetic active on  $\text{Zn}^{2+}$  sites in the bulk and show five EPR sets of equidistant peaks. Theoretical band-gap calculation suggests a predominant antiferromagnetic order in stoichiometric  $(\text{Cd}, \text{Mn})\text{GeP}_2$  but the systems with vacancies as  $(\text{Cd}, V_C, \text{Mn})\text{GeP}_2$  or  $(\text{Cd}, \text{Ge}, \text{Mn})\text{GeP}_2$  are ferromagnetic and energetically stable. These materials are of great promise for room-temperature spintronics applications.

*Keywords:* Ferromagnet; diamond-like semiconductor; room-temperature spintronics.

## 1. Introduction

Existing semiconductor electronic and optoelectronic devices employ charges of carriers under the control of electric and optical excitation. Nanotechnology calls into being further squeezing dimensions and also manipulation with inherent quantum values of electron and hole as a spin orientation. The source of ordered spins maybe arranged using ferromagnetic semiconductors or half-metals. However to inject spins effectively into a heterojunction, physical and chemical properties of the substance should be friendly and close to existing semiconductor technologies.

A few III-V and II-VI semiconductors containing Mn, Cr or Co impurities were found to show properties of ferromagnets (FM). GaMnAs layers have already been employed in spin-injecting LEDs at the operation temperature of  $\sim 50$  K.<sup>1</sup> Other promising materials as GaN:Mn and ZnO:Co show higher Curie temperature<sup>2,3</sup> but possess a hexagonal crystal structure. Wide bandgap semiconductors for spintronics were reviewed in Ref. 4. For the aim of nonscattered quantum transport through a spintronic heteronanostructure it is strongly desired to have, at our disposal, a diamond-like semiconductor material, which provides simultaneously a good conjugation with well-developed Si and GaAs wafers and a ferromagnetic state at room temperature (RT). These materials were discovered recently.<sup>5-7</sup> The closest analogs of IV and III-V semiconductors, the ternary II-IV-V<sub>2</sub> semiconductors became host materials to RT ferromagnetism in the frame of diamond-like crystal structure.

FM layers can serve as an efficient (up to 100% polarized) spin injector, meanwhile FM quantum dots as a local container of spin-polarized electrons/holes makes it possible to tunnel exchange with nearby others. Ternary chalcopyrite-type materials remain the only ones showing properties in combination of diamond-like crystal structure, RT FM and ability to form solid solutions with silicon, germanium or gallium arsenides. Additionally, they can be grown epitaxially on developed substrates of Si, III-V compounds with well matched lattices and other physical chemical coefficients.

## 2. Experimental

Single crystals of II-IV-V<sub>2</sub> semiconductors can be grown by various technological methods depending on their composition. CdGeP<sub>2</sub> and ZnGeP<sub>2</sub> single crystals were grown by directional crystallization of the stoichiometric melt and the vertical Bridgman method. The crystals were oriented by X-ray diffraction and cut along

(112) plane or perpendicular to the isotropic direction [001]. Substrates were treated in a standard manner using mechanical, chemical–mechanical polishing procedure and chemical etching to obtain a mirror-like plane. The starting CdGeP<sub>2</sub> crystals showed a compensated *n*-type and ZnGeP<sub>2</sub> crystals showed a highly resistance *p*-type conductivity. To grow Mn-containing single crystal layer of ferromagnetic chalcopyrites, the molecular beam epitaxy chamber was employed. Consecutive Mn-layer deposition and solid-phase chemical substitution reaction were accompanied with Mn-diffusion in depth. FM chalcopyrites II–IV–V<sub>2</sub>Mn were grown in various crystalline aggregative states — single crystal layers and bulks as well as polycrystalline bulk materials. To date epitaxial layers were grown by depositing Mn on single crystalline substrate and diffusing substitution at 400–550°C in MBE chamber and by metal-organic MBE technique as well. It was expected and then experimentally shown for CdGeP<sub>2</sub>, ZnGeP<sub>2</sub>, ZnGeAs<sub>2</sub> and ZnSnAs<sub>2</sub> that Mn<sup>2+</sup> substitute principally Cd<sup>2+</sup>/Zn<sup>2+</sup> sites. Minor substitution of IV-group element perhaps plays a role in a double exchange mechanism of Mn<sup>2+</sup>–Mn<sup>3+</sup> ions together with holes supplied by acceptors.

EPR spectra were measured with JEOL X-band EPR spectrometer ( $f = 9.3$  GHz) in the temperature range of  $T = 3.5 \sim 300$  K. Magnetic properties were measured using Toei type VSM-5 vibrating sample magnetometer (VSM) and Quantum Design MPMS SQUID magnetometer (SQUID) in the temperature range 80 ~ 423 K and 2 ~ 400 K, respectively.

*In situ* ultraviolet and x-ray photoemission spectral (UPS, XPS) measurements were performed at BL-18A of the Photon Factory. The total energy resolution of the spectrometer including temperature broadening was 800 meV for XPS and 200 meV for UPS. The surface was analyzed under pressure below  $7 \times 10^{-10}$  Torr and at RT. The single crystal of ZnGeP<sub>2</sub> (001) was loaded into the spectrometer and cleaned by Ar<sup>+</sup>-ion sputtering at 1.5 kV. Surface cleanliness was checked for the absence of O 1s and C 1s contaminations by XPS. Then the substrate was heated to 400°C, and Mn metal (99.999%) was deposited at a rate of 3 Å/min.<sup>8</sup> After the Mn deposition, the sample was post-annealed for 5 min and then cooled down to RT.

The first principles calculations based on the Korringa–Kohn–Rostoker coherent-potential-approximation local-density-approximation (KKR-CPA-LDA) method were conducted to investigate electronic and magnetic structure of chalcopyrites heavily-doped with manganese.

### 3. Results and Discussion

The high quality crystal of ZnGeP<sub>2</sub> grown for nonlinear optics was used as a reference sample. It was intentionally undoped with a light excess of off-stoichiometric germanium confirmed by X-ray diffraction. The crystal oriented in [001] and [011] directions showed a set of EPR peaks characteristic of that observed earlier for stable point defects in ZnGeP<sub>2</sub>. Figure 1 presents the EPR spectra recorded in undoped ZnGeP<sub>2</sub> substrate for three orientations: parallel and perpendicular to

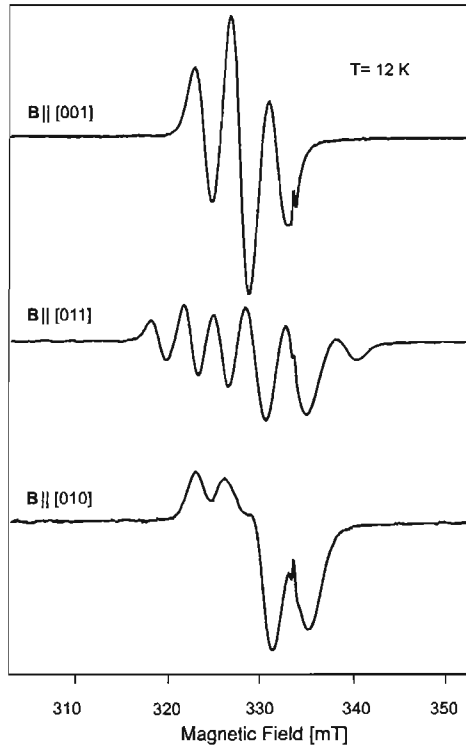


Fig. 1. EPR spectra of the reference undoped  $\text{ZnGeP}_2$  crystal in three orientations  $\mathbf{B}||[001]$ ,  $\mathbf{B}||[011]$  and  $\mathbf{B}||[010]$ .

tetragonal c-axis and parallel to  $[011]$  direction. The spectra were established to belong to zinc vacancy  $V_{\text{Zn}}$ ,<sup>9–11</sup> and we found a remarkable concentration of these defects in our initial crystals.

To clarify a chemical state of Mn ion in  $\text{ZnGeP}_2$  with zinc vacancies, we used EPR spectra and *in situ* photoemission spectra (PES) techniques. Figure 2 presents magnetic resonance spectra for  $\text{ZnGeP}_2$  bulk crystal after Mn diffusion. The spectra are given in two reciprocal orientations  $\mathbf{B}||[001]$  and  $\mathbf{B} \perp [001]$ , and are in a good agreement with angular dependences of EPR peaks calculated for electron transitions between field split levels of Mn center, Fig. 2.  $\text{Mn}^{2+}$  ions occur to distribute in the bulk of the chalcopyrite lattice and occupy  $\text{Zn}^{2+}$  sites. The signals due to zinc vacancies  $V_{\text{Zn}}$  and manganese ions  $\text{Mn}^{2+}$  are overlapped partly, but different temperature dependencies of the peaks allow their resolution distinctly. There is evidence that some broad lines with temperature dependent positions exist in the range of  $T = 4$  to 280 K and seem to belong to a resonance due to a strong magnetic ordering.<sup>12</sup> Signals like ferromagnetic resonance lines are much intense as compared to EPR lines and can be observed even in a micron thick film of ferromagnets. This gave us the experimental chance to observe FM resonance for samples with a sufficient volume of FM matter. For homogeneously doped bulk  $(\text{Zn}, \text{Mn})\text{GeP}_2$  crystals,

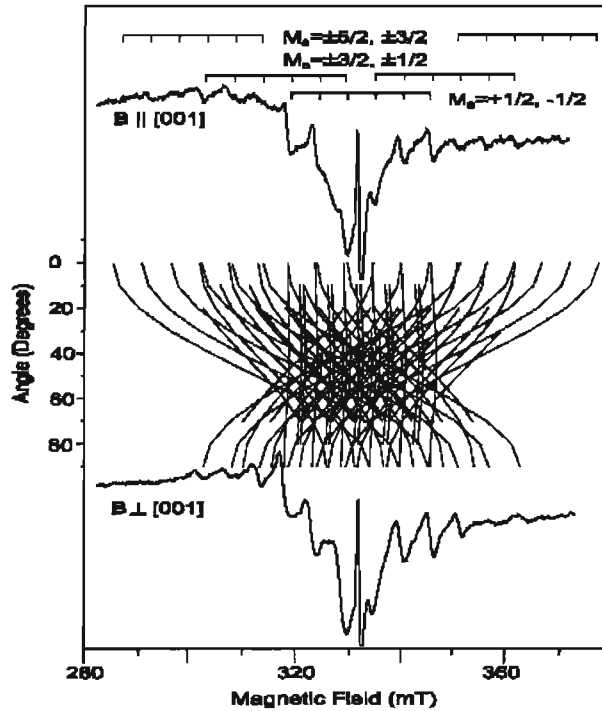


Fig. 2. EPR spectra at  $T = 4$  K for  $\text{Mn}^{2+}$  ion in the bulk  $\text{ZnGeP}_2:\text{Mn}$  crystal as a result of diffusion. Two reciprocally perpendicular orientations of the single crystal (experiment) and angular dependence of EPR  $\text{Mn}^{2+}$  related signals (calculation). Sets of equidistant peaks appear only after the growth of  $(\text{Zn}, \text{Mn})\text{GeP}_2$  layer on  $\text{ZnGeP}_2$  single crystal.

the presence of two nonequivalent isolated manganese centers in the chalcopyrite crystal lattice has been found recently.<sup>13</sup>

Well-defined magnetic hysteresis curves were observed in  $\text{CdGeP}_2:\text{Mn}$  and  $\text{ZnGeP}_2:\text{Mn}$  systems as shown in Figs. 3 and 4. For thin film layers produced by Mn diffusion, the magnetization  $M(H)$  is typical for ferromagnets and remains up to 423 K and 350 K, respectively.<sup>7,14,15</sup> Experiments also demonstrate that the main FM phases for both  $\text{CdGeP}_2:\text{Mn}$  and  $\text{ZnGeP}_2:\text{Mn}$  chalcopyrite systems show an abrupt temperature dependence of magnetization  $M(T)$  with the Curie temperature obtained by extrapolation to zero as high as  $T_C = 310 \sim 320$  K.

*In situ* ultraviolet and x-ray photoemission measurements were performed at BL-18A of the Photon Factory.<sup>8</sup> Mn metal of the nominal thickness 150 Å was deposited onto the  $\text{ZnGeP}_2$  single-crystal surface annealed at 400°C. Spectra were taken while the synthesized  $\text{ZnGeP}_2:\text{Mn}$  layer was gradually  $\text{Ar}^+$ -sputter-etched (1.5 kV). Figure 5 shows the relevant core-level spectra taken in the sputtering series. The sputtering ratio was roughly estimated to be 2 Å/min. The as-prepared surface shows Ge and P signals as well as Mn signals. The Ge and P signals were observed even for the nominal 500 Å Mn-deposition (not shown), indicating the

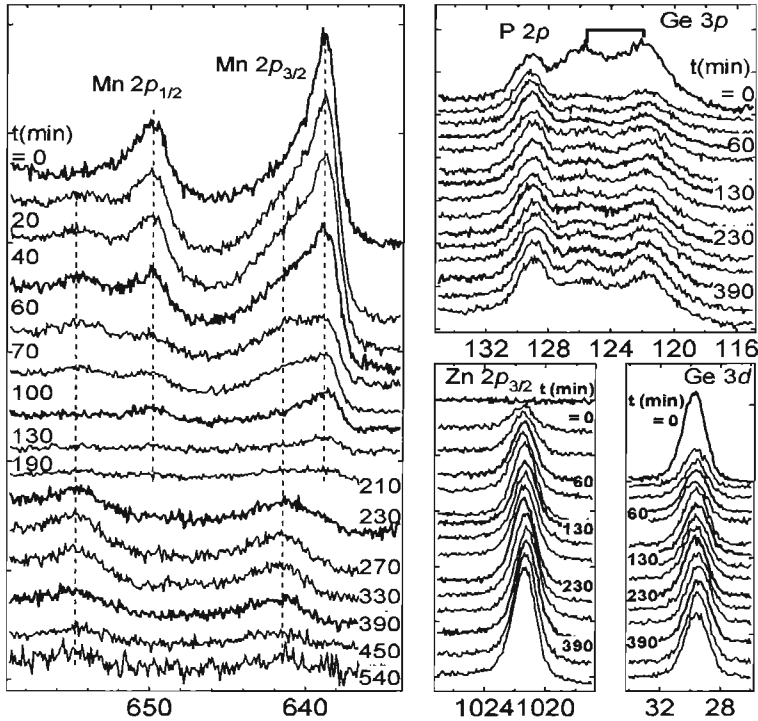


Fig. 5. Photoelectron spectra of core levels of relevant atoms measured *in-situ* during the sputtering process after deposition of Mn (nominally 15 nm in thickness) onto ZnGeP<sub>2</sub>.

out-diffusion of Ge and P atoms to the surface region. The line-shape and the energy position of the Mn 2p core-level spectrum is that of a metallic Mn compound, indicating that the compound in the surface region is a metallic Mn compound. The data suggest different Mn compounds and the peak at  $E_B = 641.6$  eV is attributed to the divalent signal of a DMS-like compound. After 100 min sputtering and removing the intermediate sub-surface layer, the matrix of Zn, Ge, and P has come to the chalcopyrite structure with Mn incorporated in it. After 230 min sputtering, only the divalent Mn signal is observed, the intensity of which decreases systematically until the Mn signal finally disappears. During the whole sputtering series, no signal at  $E_B = 639.2$  eV, which is the peak position of Mn 2p<sub>3/2</sub> of MnP, was observed. From this, we excluded the possibility of MnP ( $T_C = 290$  K) being the origin of the room-temperature ferromagnetism.

The origin of the ferromagnetism in DMSs has been investigated using the first-principles electronic structure calculations by Akai *et al.*<sup>16</sup> In these systems, the effective exchange interactions are mainly determined by the competition between the double-exchange and super-exchange interactions. The electronic structure calculation based on the local density approximation (LDA) usually takes into account the basic process producing the double-exchange and super-exchange, which makes

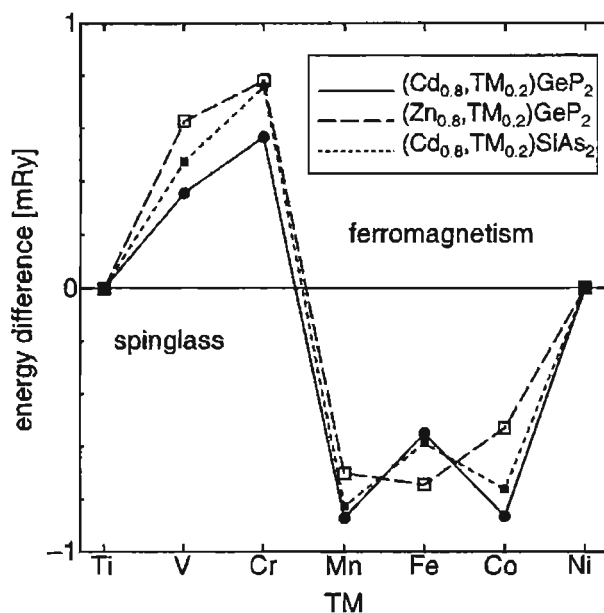


Fig. 6. Energy difference between the ferromagnetic state and the spinglass-like state in II-IV-V<sub>2</sub> chalcopyrite DMSs with transition metals Ti, V, Cr, Mn, Fe, Co and Ni.

it possible to discuss the magnetic structure of the system semi-quantitatively. To examine the relative stability of the magnetic states, the total energy difference between the FM and spinglass-like states were calculated.<sup>17</sup>

When Cd or Zn atoms are substituted by Mn atoms, the ground state magnetic structure is spinglass-like. This result is consistent with previous calculation by Zhao *et al.*<sup>18</sup> This is because *d*-states are nearly half-filled and the super-exchange prevails. On the other hand if Mn atoms substitute Ge atoms, the system becomes ferromagnetic due to the double-exchange involving *d*-holes. However, the calculation of the formation energies shows that the latter is not energetically favorable. Figure 6 demonstrates the results of calculation<sup>17</sup> for CdGeP<sub>2</sub>, ZnGeP<sub>2</sub> and CdSiAs<sub>2</sub> doped with transition metal (TM) impurities on II-element site. TM concentrations are fixed to 20%. The positive energy difference indicates that the ferromagnetic state is stabler than spinglass-like state. As shown in the figure, though the ferromagnetic states are stable in (Cd, V)GeP<sub>2</sub> and (Cd, Cr)GeP<sub>2</sub>, other impurities as Mn, Fe, Co result in the spinglass-like ground states. Ti and Ni atoms in CdGeP<sub>2</sub> could not have the magnetic moment. All the descriptions are applicable to ZnGeP<sub>2</sub> and CdSiAs<sub>2</sub> chalcopyrite compounds.

It is shown that the system with vacancies (Cd, V<sub>c</sub>, Mn)GeP<sub>2</sub> or nonstoichiometric (Cd, Ge, Mn)GeP<sub>2</sub> are also FM and energetically favorable compared with other systems. Figure 7 shows the energy difference between the ferromagnetic and spinglass-like state as a function of the vacancy concentration. The positive  $\Delta E$

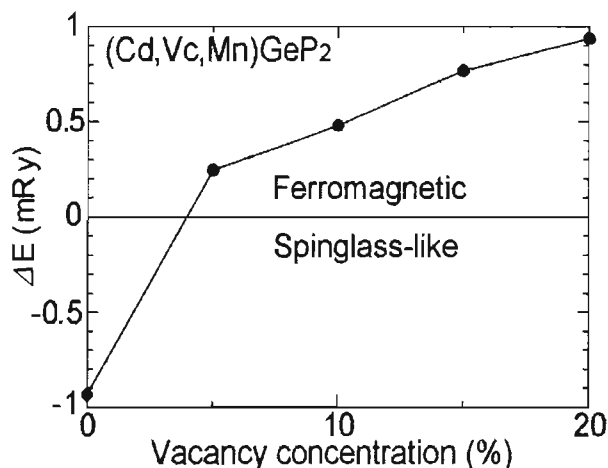


Fig. 7. Relative stability of the spinglass-like state against the ferromagnetic state for  $(\text{Cd}_{0.8-x}\text{Mn}_{0.2}\text{Vc}_x)\text{GeP}_2$ .

means that FM state is more stable than the spinglass-like state at reasonable concentrations of vacancies. The result for Ge-rich material is consistent with Mahadevan and Zunger's model.<sup>19</sup> Though we do not exclude the possibility that some other unknown magnetic phases exist in the matrix, we conclude at the moment that the above two are the most plausible candidates for the FM phase observed experimentally in  $\text{CdGeP}_2:\text{Mn}$ . We come to the same conclusion also for  $\text{ZnGeP}_2:\text{Mn}$ , i.e., the existence of  $(\text{Zn}, \text{Vc}, \text{Mn})\text{GeP}_2$  or  $(\text{Zn}, \text{Ge}, \text{Mn})\text{GeP}_2$  seem to be the origin of the ferromagnetism of  $\text{ZnGeP}_2:\text{Mn}$ . The existence of Zn vacancies in undoped and Mn-doped  $\text{ZnGeP}_2$  has been observed experimentally.

#### 4. Conclusion

Sample preparation and characterization of novel chalcopyrite-based magnetic semiconductors  $\text{CdGeP}_2:\text{Mn}$  and  $\text{ZnGeP}_2:\text{Mn}$  are summarized. In both materials, ferromagnetic properties have been observed up to temperatures considerably higher than room temperature. EPR found divalent Mn ions in the bulk due to in-diffusion. *In situ* photoelectron spectroscopy revealed that the surface layer of  $\text{ZnGeP}_2:\text{Mn}$  is metallic while sub-surface layer is nonmetallic with well-defined  $\text{Mn}^{2+}$  signals, typical of DMS states. *Ab initio* calculation of the electronic and magnetic states of  $\text{ZnGeP}_2:\text{Mn}$  was performed. Ferromagnetic state in Mn-doped chalcopyrites is concluded to become stable in the presence of vacancies or point defect nonstoichiometry. The existence of zinc vacancies of a remarkable concentration in  $\text{ZnGeP}_2$  and  $(\text{Zn}, \text{Mn})\text{GeP}_2$  was proved by EPR experiments that supports the theoretical model employing vacancies for the explanation of FM state in chalcopyrites.

Ternary semiconductor compounds  $\text{CdGeP}_2:\text{Mn}$  and  $\text{ZnGeP}_2:\text{Mn}$  represent a source of the novel FM materials based on II-IV-V<sub>2</sub> chalcopyrites with the Curie



point above RT. Since the crystal structure of novel FM compounds belongs to the diamond-like crystal family and the Bravais lattice of them as well as of GaAs-type and Si-type materials is the same (chalcopyrite, sphalerite, diamond), we accent here the FM semiconductor chalcopyrites are of great promise to the development of epitaxial layers injecting strongly spin-polarized carriers and nanosized FM objects on RT devices within established silicon and III-V technologies.

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