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Room temperature visible-light electroluminescence in Mn doped semiconductors

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Light emissions due to the d-d transitions of transition-metal (TM) doped in semiconductors are promising because they can occur in indirect band-gap semiconductors, where the band-gap emission is not effective. Electroluminescence (EL) due to the d-d transitions have been realized in TM-doped II-VI wide-gap semiconductors, such as ZnS:Mn, by applying a high electric field (10^6 V/cm) directly to a ZnS:Mn crystal. Under this high electric field, electron carriers are accelerated to sufficiently high energy, such that these hot electrons can excite the Mn^{2+} atoms by impact excitations. However, EL due to the d-d transitions of TM atoms doped in more widely used semiconductors, such as GaAs and Si, has not been realized so far. Because of the high conductivity of TM-doped GaAs and Si, it is impossible to apply a high electric field directly to them in the same manner as was done to ZnS:Mn.

Here, we demonstrate visible-light EL due to the d-d transitions of TM in light-emitting diodes (LEDs) with GaAs:Mn [1] and Si:Mn [2], in the temperature range from 4 K to room temperature. We design p^+-n junctions containing a p^+ GaAs:Mn or Si:Mn layer, in which at a reverse bias voltage (-3 to -6 V), an intense electric field (~10^6 V/cm) builds up in the depletion layers of the p^+-n junctions. Holes are injected to the depletion layer by Zener tunneling from the conduction band or by diffusion of minority holes from the valence band of the n-type layer. These holes are accelerated to sufficiently high energy by the intense electric field in the depletion layer, and excite the d electrons of Mn in the p+ GaAs/Si:Mn layer by impact excitations when they exit the depletion layer (Fig. 1). In GaAs:Mn based LEDs, we observe visible-light (reddish-yellow) emission at E_1 = 1.89 eV and E_2 = 2.16 eV, which are exactly the same as the ${}^4T_1$(4G) → ${}^6A_1$(6S) and ${}^4A_2$(4F) → ${}^4T_1$(4G) transition energy of the Mn ions in ZnS [3]. In Si:Mn based LEDs, we observe visible-light emission at E_1 = 1.75 eV and E_2 = 2.30 eV. For both the GaAs:Mn and Si:Mn based LEDs, the threshold voltage for the observation of visible-light EL is -4 V, corresponding to $-(E_1+E_2)/e$. This indicates that the impact excitation is most effective for the one step excitation from the ground state ${}^6A_1$(6S) to the highest excited state ${}^4A_2$(4F), while the light emission occurs by two step transitions between ${}^4A_2$(4F), ${}^4T_1$(4G), and ${}^6A_1$(6S). Furthermore, we show digital data transmission using direct amplitude modulation of our LEDs at room temperature, up to 1 Mbps, which is limited only by the RC time constant of our LEDs.

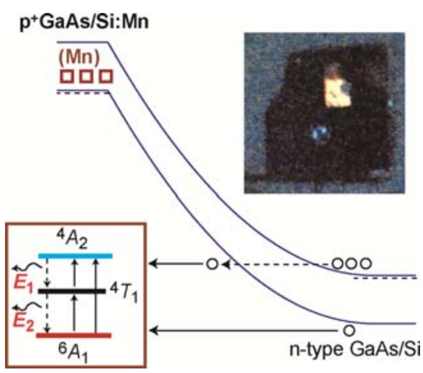

Fig. 1. Schematic band structure of a p^+-n junction LED with a Mn doped p^+ layer. The down-left inset shows the impact excitation and light-emission process of the Mn d electrons. The up-right inset shows a color picture of a Si:Mn-based LED when biased with a voltage of −4.7 V and a current density of −7.5 A/cm^2 at 300 K.

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Refs: [1] P. N. Hai, D. Maruo, M. Tanaka, Appl. Phys. Lett. **104**, 122409 (2014). [2] P. N. Hai, D. Maruo, L. D. Anh, M. Tanaka, JSAP 2014 Spring meeting 19p-E7-10. [3] T. Kushida *et al.* J. Phys. Soc. Jpn. **37**, 1341 (1974).