

From our readers

SELF-ORGANIZED GROWTH CONTROLLED BY CHARGE STATES OF MAGNETIC IMPURITIES

To the editor – The exploitation of strain fields, generated by the lattice mismatch at interfaces of heterostructures, has been successfully used in the self-organized growth of quantum dots¹. Further progress in this direction could boost the development of high-density three-dimensional memories and spatial light modulators for advanced photonic applications². We argue here that Coulomb forces between the constituents of semiconductor alloys may also be used to control the deposition of nanocrystals.

Certain alloy phase diagrams exhibit a solubility gap, where no homogenous growth is possible, leading to spinodal decomposition into regions with low and high concentrations of a particular constituent. In cases where the concentration of one of the constituents is small, this could lead to the formation of coherent nanocrystals within a majority phase. For instance, such spinodal decomposition is known to occur in epitaxially grown (Ga,In)N, where In-rich quantum-dot-like regions are embedded within an In-poor matrix. Pioneering *ab initio* calculations by van Schilfgaarde and Mryasov³ as well as others⁴ have revealed a particularly strong tendency of diluted magnetic semiconductors (DMS) to form non-random alloys.

Spinodal decomposition does not involve the precipitation of another crystallographic phase, and therefore is not easy to detect experimentally. Nevertheless, it has been observed in electron transmission microscopy in (Ga,Mn)As, where coherent zincblende Mn-rich (Mn,Ga)As nanocrystals^{5,6} led to an apparent Curie temperature of 360 K. Furthermore, a synchrotron radiation microprobe examination⁷ revealed the presence of Mn-rich nanocrystals in the host hexagonal structure of (Ga,Mn)N. It is therefore reasonable to speculate that coherent nanoclusters with a large concentration of the magnetic constituent could account for the high apparent Curie temperatures in (Ga,Mn)N and related systems. This could explain the longstanding puzzle concerning the origin of the ferromagnetic response of diluted magnetic semiconductors and oxides, in which no foreign crystallographic phases are detected but the average concentration of magnetic ions is far below the percolation limit for the nearest-neighbour coupling, and at the same time the free-carrier density is too low to mediate an efficient long-range exchange interaction. Remarkably, the presence of ferromagnetic nanocrystals leads to an enhanced magneto-optical⁶ and magnetotransport⁸ response. This opens the door for various applications of such hybrid systems, including aforementioned magneto-optical spatial light modulators for volumetric recording, provided that methods for controlling the properties of the nanocrystal growth could be found.

It is known that the energy levels derived from the open *d* shells of transition metals reside usually in the bandgap of the host semiconductor. This property is already exploited for the fabrication of semi-insulating materials, in which mid-gap levels of magnetic impurities trap carriers originating from residual impurities or defects. The essential point of our argument is the observation that such a trapping alters the charge state of the magnetic ions and hence affects their mutual Coulomb interactions. These interactions are not screened out in materials with small carrier concentrations, and we argue therefore that the intersite Coulomb repulsion overcompensates the lowering of the free energy due to the nearest-neighbour bonding. This impedes the spinodal decomposition and stabilizes the growth of a uniform alloy even if the concentration of the constituents lies within the solubility gap for the *isoelectronic* compound. Accordingly, intentional co-doping of DMS with shallow acceptors or donors could provide a means for successfully controlling the ion aggregation during epitaxy.

It is evident that the theory suggested here should apply to a broad class of DMS as well to semiconductors and insulators, in which a constituent, dopant, or defect can exist in different charge states under various growth conditions. As important examples we consider (Ga,Mn)N and (Zn,Cr)Te, in which remarkable changes in ferromagnetic characteristics on co-doping with shallow impurities have recently been reported^{9,10}. In particular, a strong dependence of saturation magnetization M_s at 300 K on co-doping with Si donors and Mg acceptors⁹ has been found for (Ga,Mn)N with an average Mn concentration of about 0.2%. Similarly, ferromagnetism of (Zn,Cr)Te with Cr concentrations above 1% is destroyed by N-acceptor doping¹⁰. Both double exchange and superexchange are inefficient at the low transition metal concentrations and for the mid-gap transition metal levels in question. At the same time, the model of nanocrystal self-organized growth invoked here explains readily why ferromagnetism appears when transition metal impurities are in the neutral charge state, and vanishes when co-doping by the shallow impurities cause the transition metal atoms to be electrically charged.

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