Mendeleev Commun., 2027, **37**, JUST ACCEPTED

Received 21.07.26 26/8154

Revised 31.08.26

3d transition metal ion implanted GaN probed by XPS

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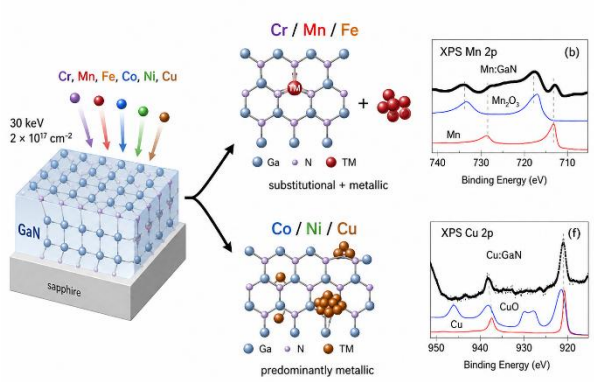
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DOI: 10.71267/mencom.8154

The results of XPS measurements of the core level and valence band spectra of GaN implanted with 3d-metal ions (Cr, Mn, Fe, Co, Ni, Cu) at an energy of 30 keV and an irradiation dose of $2x10^{17}$ cm^{-2} are presented. It was found that implantation of GaN with Fe, Mn, and Cr ions results in both Ga substituted and embedded to interstitials atoms while implantation with Co, Ni, and Cu ions leads to the formation of only embedded atoms with the formation of clusters and nanoparticles of metals.



Keywords: XPS, ion implantation, gallium nitride, cation substitution, transition metals.

Gallium nitride is one of the most promising wide-bandgap semiconductors, finding widespread application in optoelectronics,[1] power electronics,[2] and microwave devices[3] due to its high melting point, wide bandgap, and high electron mobility.[4]

Of particular interest is the possibility of imparting magnetic properties to GaN by doping with transition metal ions (TM) to create diluted magnetic semiconductors (DMS).[5,6] These materials combine the semiconducting properties with magnetic ordering, opening up prospects for spintronics.[7]

Ion implantation is one of the most flexible and technologically controllable methods for introducing impurities into the semiconductor matrices.[8–10] This method has proven highly effective for studying the potential DMS systems.[11,12] Unlikepitaxial growth methods, implantation allows precise control of the dose, distribution profile, and implantation depth of ions, as well as doping of already formed structures.[13] The pulsed ion sources based on a vacuum metal vapor arc enable high fluences to be achieved at relatively low ion energies, opening up the possibility of creating DMS structures with high concentrations of magnetic impurities.[14]

A key challenge in creating GaN-based DMS is determining the chemical state of the implanted ions and their effect on the matrix structure. X-ray photoelectron spectroscopy (XPS) allows for the identification of chemical bonds, determination of the charge states of impurities, and detection of secondary phases or clusters.[15,16] As demonstrated in several studies, XPS analysis allows for distinguishing between the substitutional and interstitial positions of transition metal ions.[17,18] Furthermore, the XPS valence band spectra can reveal features of the hybridization of the TM 3d and N 2p states.

In this study, we studied GaN thin films† implanted with 3d transition metal ions (Mn, Fe, Co, Ni, Cr, Cu) using a pulsed vacuum arc ion source. A comparative analysis of the survey and core XPS spectra, as well as the valence band spectra, was performed to identify the features of the chemical state of the implanted ions and their influence on the electronic structure of the matrix.[19]

† Briefly, the GaN samples were obtained using the sol-gel method on AlN/sapphire substrate. The film thickness was about 300 nm. Thin films were implanted with 3d TM ions (Cr, Mn, Fe, Co, Ni, and Cu) using a metal vapor vacuum arc ion source. The operating pressure in the implantation chamber was no worse than 2.0×10^2 Pa. The ion energy was 30 keV, the pulse duration was 0.4 ms, with a current density of 0.6 mA/cm^2 and an ion fluence of 2×10^{17} cm^{-2}. To ensure the lateral homogeneity of the implanted ions within the matrix material, the ion beam was defocused.

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Fig. 1 shows the survey XPS spectra of ion-implanted GaN samples. The data obtained demonstrate the high chemical quality of the studied samples, as the spectra do not contain signals from uncontrolled impurities.

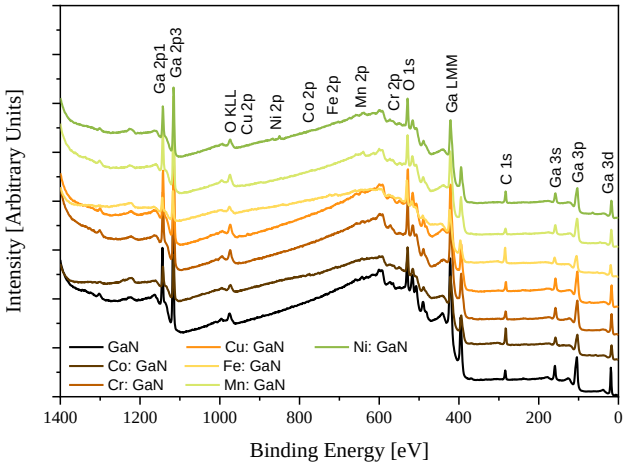


Figure 1 XPS survey spectra of GaN implanted with 3d-metal ions.

XPS TM 2p spectra of Cr, Mn, and Fe doped Ga (Fig. 2) show two set of lines, one of which corresponds to substituted 3d-ions and another one is close to that of pure metals. These data clearly show the existence of substituted (Me→Ga) and embedded (to interstitials) impurity atoms in the GaN lattice. On the other hand, in XPS TM 2p spectra of Co, Ni, and Cu doped GaN, only one set of lines is observed, which is close to that of pure metals. This means that, in this case, the substitution is less favorable and the formation of TM–N bonds is very unlikely. It is possible that, for this reason, the formation of Co, Ni and Cu nitrides is difficult.

The discovered division of 3d elements into two groups based on their behavior in the GaN lattice has a thermodynamic and crystal-chemical justification.[20,21] For Cr, Mn, and Fe, substitution of the Ga cation is energetically favorable due to their relatively small ionic radii in the high-spin state (especially for Cr^{3+} and Fe^{3+}), close to that of Ga^{3+} (0.62 Å for the tetrahedral coordination), as well as the significant negative energy of formation of the corresponding nitrides.[22–24] Furthermore, the partially filled 3d shells of these elements ensure the strong covalent hybridization with N 2p states, which reduces the total energy of the system when inserted into Ga sites.[25] In contrast, Co, Ni, and Cu are characterized by higher electronegativity and a less pronounced affinity for nitrogen.[26] For Cu, Co, and Ni, the formation of nitrides could be unfavorable or have lower binding energies.[27]

These results are consistent with measurements of XPS valence band spectra (Fig. 3), which in all cases show the presence of additional high-energy subbands that are absent in the spectrum of undoped gallium nitride and therefore can be attributed to the formation of metallic clusters. However, the shape of this contribution differs significantly: for Cr, Mn, and Fe, a broad incoherent structure is observed, interpreted as a superposition of hybridized TM 3d / N 2p states (substituted ions) and the metallic component (interstitial clusters). For Co, Ni, and Cu, by contrast, a sharp peak at E_F, typical of the itinerant electrons in metallic nanoparticles, dominates. The structure of the main part of the valence band practically replicates that of GaN, indicating the absence of significant overlap of wave functions between the impurity clusters and matrix.

Thus, only in the samples containing Cr, Mn, and Fe are conditions created for the formation of a dilute magnetic semiconductor with ions at cation sites, where exchange interactions via nitrogen can lead to ferromagnetic ordering at sufficiently high concentrations. In contrast, for Co, Ni, and Cu, magnetism is determined by the superparamagnetic behavior of individual clusters, which prevents the formation of the uniform magnetic phase required for spintronic applications.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation (project FEUZ-2026-0010).

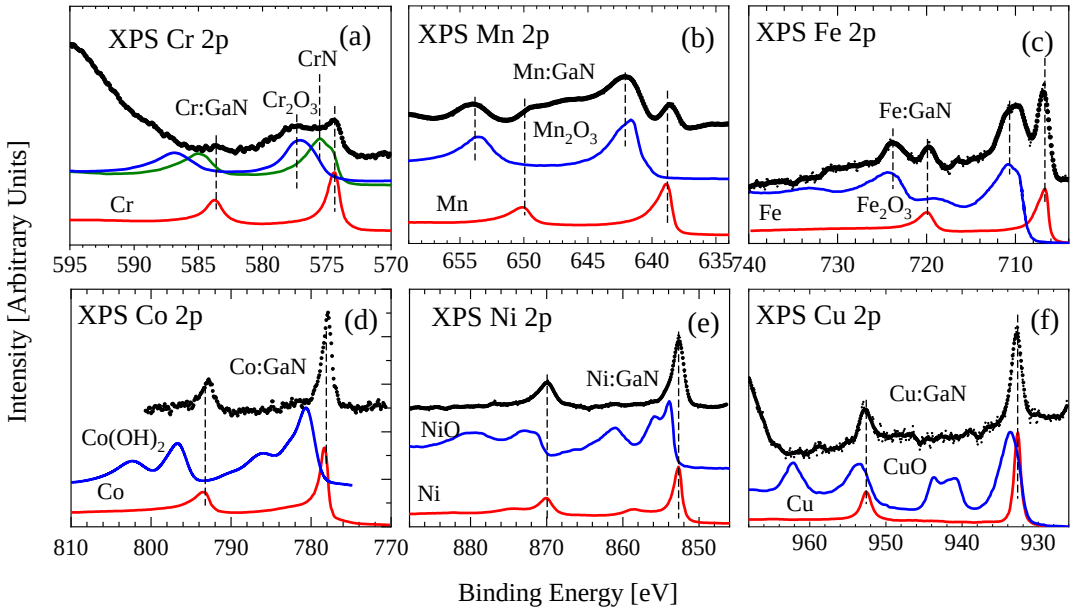


Figure 2 XPS Me 2p-spectra of GaN:3d: (*a*) Cr, (*b*) Mn, (*c*) Fe, (*d*) Co, (*e*) Ni, (*f*) Cu. Experimental curves are shown as black dots.

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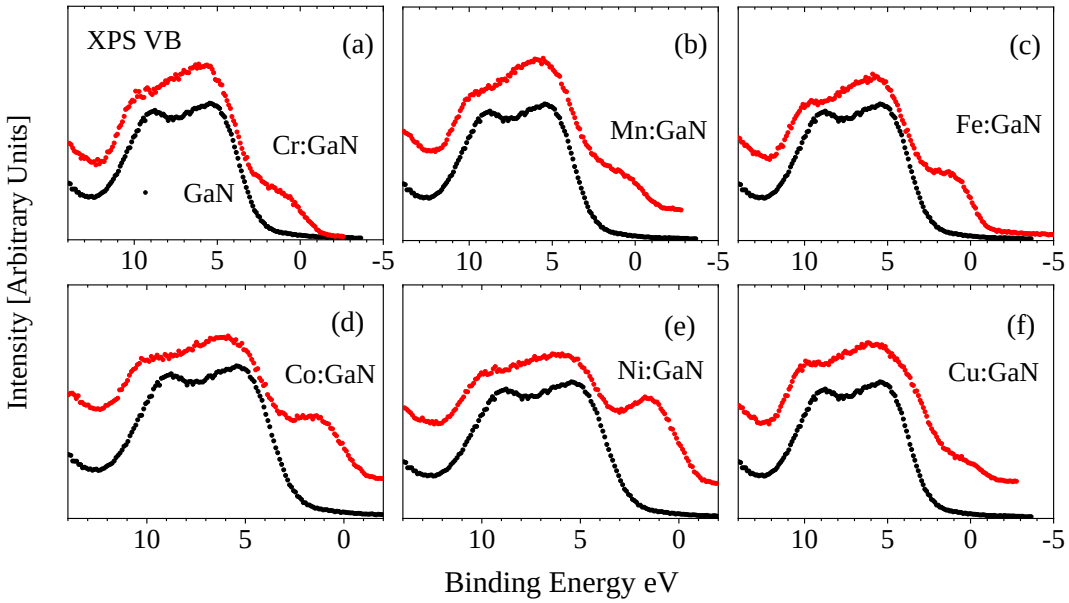


Figure 3 XPS valence band spectra of GaN:3d: (*a*) Cr, (*b*) Mn, (*c*) Fe, (*d*) Co, (*e*) Ni, (*f*) Cu.

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Received: 21st July 2026; Com. 26/8154

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