

Electronic properties of (Zn,Co)O systems probed by scanning tunnelling spectroscopy

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Abstract – *The aim of this paper is to gain insight into the electronic properties of (Zn,Co)O system - a wide bandgap Diluted Magnetic Semiconductors (DMS) showing room temperature (RT) ferromagnetism under n-type doping conditions. On the experimental side, ultra-high-vacuum scanning tunnelling microscopy and spectroscopy (STM and STS) at variable temperature (T) are used to probe the local electronic structure of the system. It is presented the map of the local density of states (LDOS) of polar ZnO surfaces. Then, it is possible to decorate (incorporate) Co atoms onto (into) the semiconductor.*

Keywords: *semiconductors, surfaces*

I. INTRODUCTION

Diluted Magnetic Semiconductors are promising candidate materials for novel spintronic devices. Indeed, they not only offer the possibility to take a simultaneous advantage of both charge and spin degrees of freedom, but also open the way to an electrical control of ferromagnetism. While recent theoretical work demonstrated that RT ferromagnetism could be achieved in p-type DMS [1], a series of intriguing models emerged to explain the ferromagnetic behaviour in n-type DMS [2,3].

II. POLAR ZnO SURFACES

ZnO crystallizes in the wurtzite structure, which lacks inversion symmetry. Cleaving ZnO single crystals perpendicular to the c-axis creates the polar Zn-terminated (0001) and O-terminated (000-1) surfaces on either sides of the crystal. The stability of the polar ZnO surfaces is hotly debated. According to the ionic model [4], if the Zn (O)-terminated surface is positively (negatively) charged, a counter-field is created that compensates the macroscopic dipole moment. Several mechanisms are usually invoked to explain the stability of polar ZnO surfaces: charge transfer between the two faces thanks to metallic surface states, surface reconstructions, removal of surface atoms, chemisorption of charged impurities. Wander *et al.* [5] studied the stability of ZnO polar surfaces using ab-initio calculations and X-ray diffraction (XRD). They concluded

that both surfaces are stable thanks to an electronic transfer mechanism of 1/2 electron per surface area between them. However this charge transfer would require partially occupied metallic bands on both surfaces, which has never been observed experimentally. According to Jedrecy *et al.* [6], fractional probability of occupancy in the topmost layer cancels the dipole moment perpendicular to the surface. Experimental evidence is provided by grazing incidence XRD [6] that site distortion as well as lattice relaxation appear on the O-terminated face in order to compensate the dipole moment. A STM analysis by Dulub *et al.* [7] revealed a high density of monoatomic step-edges and triangular pits on the Zn-terminated face. Accordingly, the O-terminated surface neutrality is restored and the dipole moment cancelled. These observations have been confirmed by Kresse *et al.* [8] using DFT calculations: while a perfect ZnO surface would show metallic behaviour, triangular pits present a gap of ~1 eV and are energetically favourable with respect to isolated Zn vacancies. Further STM studies [9] showed that the O-terminated face is much smoother than the Zn-terminated one, displaying double-layer steps whose edges are stoichiometric and therefore neutral. As no metallic surface states were observed by STS, Dulub and coworkers proposed that the O-terminated surface stability could then only lie in the saturation of O-dangling bonds by hydrogen. Other STM studies [10,11,12] revealed that more vicinal O-terminated surfaces could show a high density of steps whose edge structure alternate between straight and sawtooth.

The stability of polar ZnO surfaces is allowed by several competing mechanisms: surface reconstruction, metallic surface states, triangular pits formation and step-edge reconstructions. No clear picture of the interplay between these mechanisms and their relative importance exists so far. On Figure 1, are presented obtained STM and STS results at different *T* on Zn-terminated surfaces, showing that the electronic structure (bandgap, valence band structure) is strongly affected by step-edges and defects. Moreover, in addition to the well known 0.26 nm deep triangular defects associated to the removal of a ZnO double layer, subatomic surface pits (~0.05 nm deep) were observed corresponding to single Zn atoms vacancies. As no atomic resolution can be achieved on this wide bandgap

semiconductor, electronic excitation calculations are needed in order to interpret the dI/dV vs V curves and simulate the electronic structure of the various defects of polar ZnO surfaces.

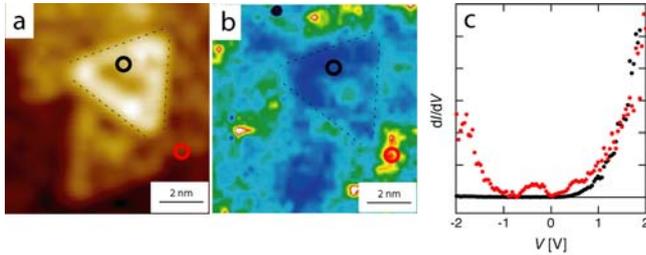


Figure 1. (a) Topography of a triangular island on a ZnO surface (Zn-terminated). (b) The corresponding low temperature (4 K) dI/dV map, measured at $V = -2$ V. (c) dI/dV vs V measured at two different positions: the red (black) curves correspond to the red (black) locations shown on panels (a) and (b)

III. INTERACTION OF Co ATOMS POLAR ZnO SURFACES

According to Zener's model [13], ferromagnetism in DMSs arises from the interaction between the magnetic moments of the transition metal ions mediated by free carriers. Based on this model, the theory recently developed by Dietl *et al.* [1] allowed to quantitatively predict the magnetic properties of DMS depending on their doping level. The most interesting prediction concerns the existence of a Curie temperature above 300 K for wide bandgap DMSs like (Ga,TM)N and (Zn,TM)O (TM = transition metal) when high p-type doping can be achieved ($p \sim 10^{20}/\text{cm}^3$). Unfortunately, due to the very high ionization potential of the p-type dopants in wide bandgap semiconductors, hole concentrations larger than $10^{18}/\text{cm}^3$ cannot be achieved. Nevertheless, several experimental studies reported Curie temperatures higher than 300 K for n-type doped (Zn,Mn)O et (Zn,Co)O [14,15]. Since then, new theories emerged to describe this electron-mediated ferromagnetism. First, Dietl *et al.* [16] proposed a new theoretical model showing that room temperature ferromagnetism in n-type doped (Zn,Co)O is due to Co nanocrystals [17]. Second, Toyoda *et al.* [18] reformulated the Korringa-Kohn-Rostoker method by including self-interaction corrections to the standard LDA approximation and demonstrated that the 3d minority spin state associated to the transition metal is not located at the Fermi level and cannot contribute to ferromagnetism unless additional electron co-doping. Third, Kittilstved *et al.* [19] showed that the ferromagnetic character of (Zn,Co)O could be switched on and off in the presence of Zn interstitials (n-type defect) and oxygen (compensating intrinsic n-type doping), respectively. Ferromagnetism in (Zn,Co)O remains a very controversial topic. What is clearly missing is the identification of the local electronic structure in the vicinity of Co atoms in this system. What is not well established is the level of dilution of Co into ZnO. Indeed,

it seems that in the case thick Co films (several monolayers), Co coalescence precedes the diffusion process. I believe that theoretical spectroscopy calculations are a unique tool to interpret the LDOS data [dI/dV maps and dI/dV vs V curves] of (Zn,Co)O systems consisting of Co adsorbed atoms as well as Co substitutional and/or interstitials atoms into the ZnO lattice.

IV. CONCLUSIONS

In conclusion, the stability of polar ZnO surfaces is allowed by several competing mechanisms: surface reconstruction, metallic surface states, triangular pits formation and stepped reconstructions. The combination of STM/STS measurements and theoretical simulations will allow to gain unique insight into the structural and electronic properties of (Zn,Co)O systems.

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