

Intrinsic versus extrinsic ferromagnetism in HfO_{2-x} and Ni:HfO_{2-x} thin filmsErwin Hildebrandt,^{1,*} Mehrdad Baghaie Yazdi,¹ Jose Kurian,¹ S. U. Sharath,¹ Fabrice Wilhelm,² Andrei Rogalev,² and Lambert Alff^{1,†}¹*Technische Universität Darmstadt, Institute of Materials Science, Alarich-Weiss-Str. 2, 64287 Darmstadt, Germany*²*European Synchrotron Radiation Facility (ESRF), BP 220, 38043 Grenoble Cedex 9, France*

(Received 26 May 2014; revised manuscript received 2 October 2014; published 30 October 2014)

We have investigated the possible evolution of an intrinsic stable ferromagnetic moment in oxygen deficient undoped and magnetically doped HfO_{2-x} thin films grown by reactive molecular beam epitaxy. Neither oxygen vacancies nor substituted Ni in combination with such vacancies results in an observable magnetic moment for a broad range of oxygen vacancy concentrations. By combining integral and element specific magnetization measurements, we show that a fluctuating deposition rate of the magnetic dopant induces extrinsic ferromagnetism by promoting the formation of metallic clusters. We suggest the element specific measurement of an induced magnetic moment at the nonmagnetic site as a proof of intrinsic ferromagnetism in diluted magnetic semiconductors.

DOI: [10.1103/PhysRevB.90.134426](https://doi.org/10.1103/PhysRevB.90.134426)

PACS number(s): 75.50.Dd, 75.50.Pp, 75.70.-i, 81.15.Hi

I. INTRODUCTION

During the last decade, diluted magnetic semiconductors (DMS) have attracted particular interest, as the combination of semiconducting and ferromagnetic properties would allow a broad variety of spintronic devices. A vast amount of different compounds has been investigated in the past, among them III-V (e.g., GaAs) and II-VI (e.g., CdTe) semiconductors doped with magnetic elements. (Ga,Mn)As is the most prominent established DMS, however, the maximum Curie temperature T_C of about 170 K is still well below room temperature [1]. Ferromagnetism has been reported in many more materials, such as ZnO and TiO_2 , but also in perovskite materials [2,3]. In particular, in substituted ZnO and TiO_2 , ferromagnetic behavior was reported with $T_C > 300$ K [4,5]. Other examples of materials with reported high- T_C ferromagnetism are cerium and magnesium oxide doped with Co [6,7]. The origin and nature of the observed ferromagnetism in a large amount of compounds is still discussed controversially. *Intrinsic* ferromagnetism as established for (Ga,Mn)As is supposed to be due to charge carrier mediated coupling of diluted magnetic moments. The second possible origin of ferromagnetism is *extrinsic* associated with (nano)clustering of magnetic impurities. Many experimental reports are based on magnetometry only, e.g., using a superconducting quantum interference device (SQUID). However, it is necessary to combine several methods, in particular, element specific ones, to unravel the origin of ferromagnetism [8].

HfO_2 as a possible diluted magnetic semiconductor has the advantage that it has already found its way into complementary metal-oxide-semiconductor (CMOS) technology as high- k dielectric [9]. In addition, it is also currently being investigated as promising CMOS-compatible material for resistive switching devices [10–13]. The observation of room-temperature ferromagnetism in undoped but oxygen deficient hafnium oxide thin films came as a surprise [14,15]. It was speculated that hybridization of an oxygen vacancy induced impurity

band with empty d states of hafnia in combination with the transfer of a fraction of these electrons into $5d$ states results in a polarization of the defect band, accounting for ferromagnetic coupling [16]. Again, a vivid discussion started in the community whether the observed ferromagnetism was of intrinsic or extrinsic origin [17]. Several studies suggested that only the combination of magnetic dopants such as Mn, Fe, Co, and Ni together with oxygen vacancies leads to ferromagnetism [18,19]. Extrinsic ferromagnetism may be due to surface enrichment as found for Co in ~ 5 at.% Co-doped thin films of hafnium oxide, or in the case of Ni doping by metallic cluster formation [20,21]. Additionally, it was shown by *ab initio* density functional theory that Hf vacancies could be a source of ferromagnetism, forming a high spin state with an associated moment of about $3.5 \mu_B$ [22].

In this study, thin films of hafnium oxide have been grown using reactive molecular beam epitaxy (RMBE) to investigate separately (i) the role of oxygen vacancies themselves on magnetism and (ii) the combination of oxygen vacancies with magnetic Ni doping.

II. EXPERIMENT

We have used reactive molecular beam epitaxy by electron-beam co-evaporation from high-purity Hf metal (99.9%, MaTecK) and nickel metal (99.995%, Chempur) to synthesize the thin films. Oxidation was achieved by means of oxygen radicals supplied by a radical source. In this way, a wide range of oxidation conditions are achieved simply by varying the gas flow through the radical source. *In situ* rate control was performed using a quartz crystal microbalance system with rate-deposition controller. 5×5 and 7×4 mm² c -cut sapphire substrates were radiantly heated up to 700 °C by a plate resistance heating system. We have used a mesh to achieve homogeneous and stable Ni evaporation at very low deposition rates. Nominal doping concentrations ranged from 4 to 60 at.% Ni with respect to Hf concentration. Structural characterization of the thin films was carried out using an x-ray diffractometer with Cu K_α radiation (Rigaku SmartLab, 9 kW) and a magnetic property measurement system was utilized to obtain magnetization data (MPMS, Quantum Design). As an

*emh@oxide.tu-darmstadt.de

†alff@oxide.tu-darmstadt.de

important additional investigation tool we have used x-ray magnetic circular dichroism (XMCD) at beamline ID12 of the European Synchrotron Radiation Facilities (ESRF) [23]. XMCD allows element specific measurement of magnetic moments, complementing the information from SQUID probing the integral moment. We have performed XMCD on Hf for two reasons: (i) due to the high x-ray energies, the whole thin film is probed, and (ii) only induced magnetic moments at the Hf site unambiguously confirm intrinsic magnetization (in contrast to extrinsic magnetic nanoclusters).

III. RESULTS AND DISCUSSION

A. Oxygen deficient HfO_{2-x} thin films without magnetic dopants

In order to study the effect of oxygen vacancies on the magnetic properties of HfO_{2-x} thin films, the oxygen flow rate supplied to the radical source has been varied from 0.3 sccm (standard cubic centimeters per minute) to 2.5 sccm, covering a wide range of x in HfO_{2-x} . A systematic decrease of band gap by more than 1 eV and an increase of conductivity by several orders of magnitude has been observed with variation of oxygen vacancy concentration [24–26]. We have excluded by secondary ion mass spectroscopy (SIMS) that magnetic impurities such as Fe, Co, or Ni are present in the hafnium metal source. As-deposited films were also investigated by SIMS to exclude cross contamination yielding the same result. Magnetization data were obtained using a SQUID magnetometer in the range of ± 6 T at 5 and 300 K. For all samples, a clean diamagnetic behavior has been observed with no traces of ferromagnetism, regardless of oxygen vacancy concentration, and irrespective of measurement temperature. This has been confirmed by x-ray absorption by measuring the Hf XMCD signal at the $L_{2,3}$ edges. As shown in Fig. 1, there is no magnetization at the Hf site observable. Note the extraordinary low experimental error bar in XMCD intensity of ± 0.0002 .

B. Synthesis and SQUID results of Ni-doped HfO_{2-x} thin films

We have combined the controlled introduction of oxygen vacancies with the additional magnetic dopant Ni. Figure 2 shows exemplarily the diffraction pattern of a hafnium oxide

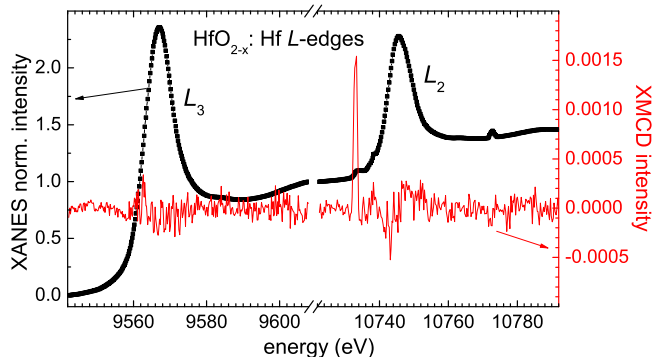


FIG. 1. (Color online) Normalized XANES (left-hand axis) and XMCD (right-hand axis) spectra at Hf $L_{2,3}$ edges of a typical HfO_{2-x} thin film recorded at 300 K and under an applied magnetic field of 6 T. The large peak in the XMCD signal is a diffraction peak.

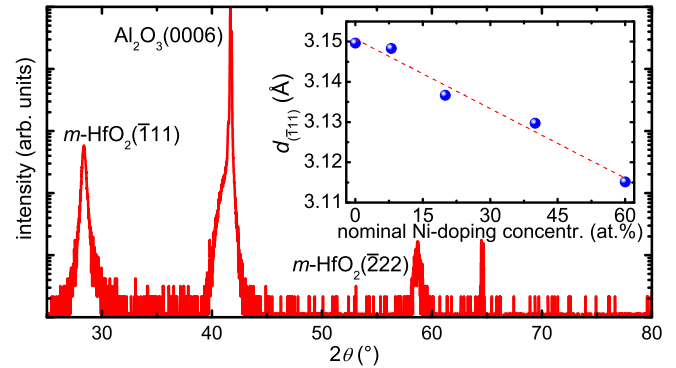


FIG. 2. (Color online) X-ray diffraction pattern of a hafnium oxide thin film doped with nominally 8 at.% Ni on c -cut sapphire. (Inset) Variation of $d_{(111)}$ with increasing nominal dopant concentration. The line is a guide to the eye.

thin film grown on c -cut sapphire with nominal 8 at.% Ni concentration. Besides the (0006) substrate reflection of Al_2O_3 at $2\theta = 41.670^\circ$, only the $(\bar{1}11)$ reflection of $m\text{-HfO}_2$ is observed at $2\theta = 28.326^\circ$. Parasitic phases such as Ni or NiO could not be observed by x-ray diffraction in none of the films. SIMS measurements confirm the physical incorporation of Ni into the films. With increasing dopant concentration, the $(\bar{1}11)$ reflection shifts towards higher angles in 2θ , corresponding to a shift in d spacing from ~ 3.15 Å for undoped hafnia to ~ 3.11 Å for nominal 60 at.% Ni dopant concentration as shown in the inset of Fig. 2. This shift clearly indicates that the slightly smaller Ni substitutes Hf in the crystal structure of $m\text{-HfO}_2$. With increasing dopant concentration a new reflection at $2\theta = 30.011^\circ$ evolves with increasing intensity, while the intensity of the $(\bar{1}11)$ reflection of $m\text{-HfO}_2$ decreases. The emerging reflection is most likely due to a tetragonal modification of substituted HfO_2 , as is the case for other substitutional elements [27,28]. The Ni solubility in HfO_2 is intrinsically limited enhancing the tendency of Ni to form metallic clusters during sample growth. Another effect of increased substitution is that $\{200\}$ reflections of $m\text{-HfO}_2$ appear, i.e., the preferential $(\bar{1}11)$ orientation is lost. While it is not possible to distinguish between substitutional Ni and Ni cluster formation, it is obvious that a part of Ni substitutes Hf within HfO_2 leading to the observed shift in lattice constants.

We have performed SQUID magnetization measurements for the whole range of oxygen vacancy and Ni doping concentrations. All measurements with one exception as discussed in the next paragraph show only diamagnetic behavior regardless of the dopant concentration. Figure 3(a) shows the magnetization obtained at 300 K for a typical film having a doping concentration of 8 at.% Ni. Note that the diamagnetic contribution of the sapphire substrate has not been subtracted. The paramagnetic contribution of Ni is too small to be separable from the large diamagnetic response of the substrate. Clearly, no ferromagnetic features have been observed irrespective of dopant concentration, oxygen content, utilized oxidation species, and deposition temperature.

When the mesh ensuring a stable Ni flow is removed, the low atomic flow and the restrictions of the feed-back loop lead to a fluctuating Ni beam. We have used this

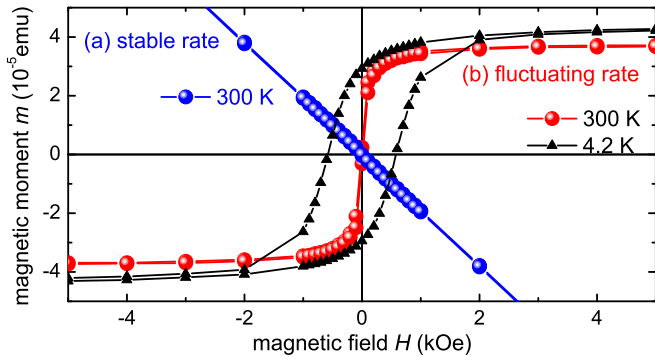


FIG. 3. (Color online) Magnetic moment vs applied field with magnetic field applied parallel to the film plane for (a) a 27-nm hafnium oxide thin film doped with 8 at.% Ni grown with stable Ni rate (diamagnetic background of Al_2O_3 has not been subtracted), and (b) a 50-nm hafnium oxide thin film doped with 8 at.% Ni grown under fluctuating rate (diamagnetic contribution of Al_2O_3 has been subtracted).

experimental condition to induce a strongly and randomly inhomogeneous Ni distribution favoring cluster formation. Figure 3(b) shows corresponding magnetization data obtained at 300 K for a 50-nm thin film of hafnium oxide grown under 2.0 sccm oxygen flow rate with nominally 8 at.% Ni doping. A ferromagnetic behavior is observable, however, with extreme low remanent magnetization and low coercive field (<50 Oe). The diamagnetic background from the sapphire substrate has been subtracted. It is evident that fluctuations in the supply of magnetic dopants enhance strongly the formation of magnetic clusters. However, a homogenous Ni flow effectively suppresses extrinsic ferromagnetism.

C. XMCD results on Ni-doped HfO_{2-x} thin films

In case of intrinsic ferromagnetism, the polarized charge carriers mediating the magnetic coupling definitely would also induce a magnetic moment at the nonmagnetic site (Hf) via the exchange path Ni-O-Hf. For example, in the ferrimagnetic double perovskites $\text{Ba}_2\text{FeReO}_6$ and $\text{Ca}_2\text{FeReO}_6$ even at the Ba and Ca sites (exchange path Fe/Re-O-Ba/Ca) a magnetic moment well above the detection limit has been observed [29]. In the case of Ni: HfO_2 , the distance between neighboring Ni and Hf moments is much closer. In contrast, if magnetism is due to magnetic cluster formation, a measurable magnetic moment at the Hf site cannot be induced through the incoherent phase boundary separating the amorphous or nanocrystalline cluster and the HfO_2 crystal, and the Ni x-ray absorption near-edge structure (XANES) should be characteristic for nickel metal. XMCD measurements have been performed with samples mounted at 15° grazing incidence geometry. The magnetic field was applied along the in-plane direction of the films, as it has been done during SQUID measurements. For the investigated samples, the $L_{2,3}$ edges of Hf and the Ni K edge were probed. Figure 4 shows XANES and XMCD data of (i) the same sample measured in SQUID [see Fig. 3(b)] and (ii) a sample deposited simultaneously in the same run but subsequently annealed at 900°C in oxygen under atmospheric pressure. As evident from Fig. 4, the XANES

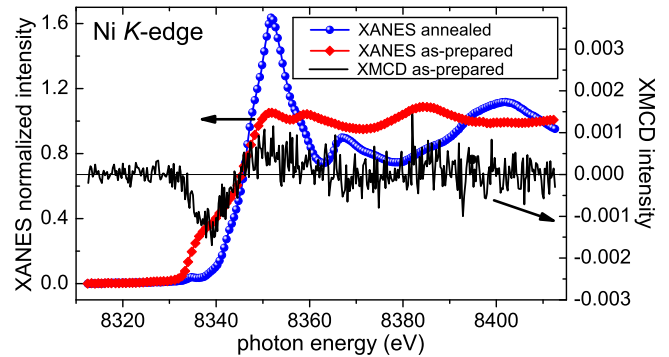


FIG. 4. (Color online) Ni K -edge XANES spectra (red and blue diamonds) for as-prepared 8 at.% Ni-doped hafnium oxide thin film grown under fluctuating rate. XMCD intensity (black curve) for the as-prepared sample measured at 300 K and 6 T.

spectrum corresponds to nickel metal for the as-prepared sample, whereas in the annealed sample NiO is identified [30]. Consequently, for the as-prepared sample, a magnetic moment at the Ni site is observed in XMCD vanishing after annealing in oxygen resulting in antiferromagnetic NiO. The XMCD observation underpins the picture that was assumed according to the growth conditions: Evaporation rate fluctuations lead to magnetic metallic nanoclusters responsible for the observed magnetic moments. Since these clusters are not observed in laboratory x-ray diffraction, we conclude that they are either amorphous or nanocrystalline and randomly oriented.

To ensure that the observed ferromagnetism is not due to any intrinsic origin, XANES and XMCD spectra were obtained at the $L_{2,3}$ edges of Hf as shown in Fig. 5. From the XANES and XMCD data, it is evident that no magnetic moment is located at the hafnium site for both films, as-prepared and post annealed in air. Thus *intrinsic* ferromagnetism can be excluded for Ni: HfO_2 . We note that the negative proof provided here cannot rigorously exclude the possibility of ferromagnetism in Ni doped HfO_2 . Conversely, we suggest the use of element specific measurements of induced magnetic moments as an important tool to provide a positive proof.

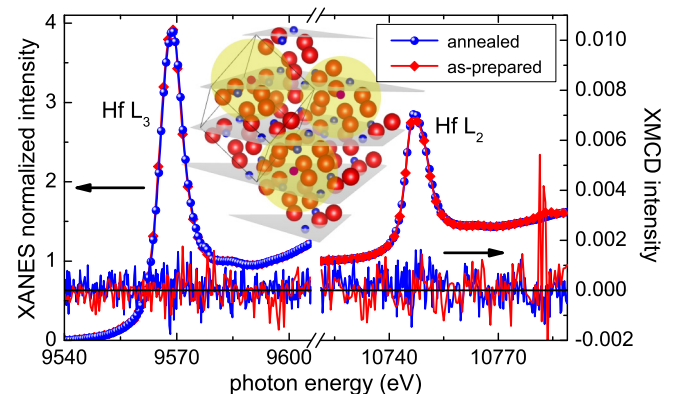


FIG. 5. (Color online) XANES of the $L_{2,3}$ edges of Hf for hafnium oxide thin films grown with fluctuating Ni source, as-prepared (red) and annealed (blue) measured at 300 K and 6 T. The inset shows the crystal structure of doped HfO_2 .

IV. CONCLUSION

We have investigated the occurrence of possible ferromagnetism in oxygen deficient undoped and magnetically doped HfO_{2-x} for a broad range of oxygen vacancy concentrations. Neither oxygen deficient HfO_{2-x} nor Ni substituted and oxygen deficient HfO_{2-x} give rise to an intrinsic ferromagnetic moment at any oxygen vacancy concentration. However, rather subtle synthesis variations, such as a fluctuating magnetic dopant source, lead to the formation of magnetic clusters with a room-temperature ferromagnetic moment. In the case of Ni doped HfO_{2-x} , this magnetic moment is clearly due to metallic Ni from amorphous or nanocrystalline clusters, i.e., it is of extrinsic origin. Only the combination of integral and element

specific magnetization measurement methods reveals the full picture of magnetism for the heavily debated oxide diluted magnetic semiconductors. In particular, the observation of an induced magnetic moment at the nonmagnetic crystal site (here Hf) can be considered as a proof of intrinsic ferromagnetism.

ACKNOWLEDGMENTS

We acknowledge Stefan Flege for carrying out SIMS measurements and Wolfgang Donner (both TU Darmstadt) for useful discussions. This work was supported by DFG through Grant No. AL 560/13-1, by the LOEWE-Centre AdRIA, by ENIAC within the project PANACHE and by BMBF (project No. 16ES0250).

-
- [1] T. Jungwirth, J. Sinova, J. Mašek, J. Kučera, and A. H. MacDonald, *Rev. Mod. Phys.* **78**, 809 (2006).
- [2] R. Janisch, P. Gopal, and N. A. Spaldin, *J. Phys.: Condes. Matter* **17**, R657 (2005).
- [3] W. Prellier, A. Fouchet, and B. Mercey, *J. Phys.: Condens. Matter* **15**, R1583 (2003).
- [4] M. Venkatesan, C. B. Fitzgerald, J. G. Lunney, and J. M. D. Coey, *Phys. Rev. Lett.* **93**, 177206 (2004).
- [5] V. R. Singh, K. Ishigami, V. K. Verma, G. Shibata, Y. Yamazaki, T. Kataoka, A. Fujimori, F.-H. Chang, D.-J. Huang, H.-J. Lin, C. T. Chen, Y. Yamada, T. Fukumura, and M. Kawasaki, *Appl. Phys. Lett.* **100**, 242404 (2012).
- [6] Y. Q. Song, Q. H. Yang, H. W. Zhang, L. Peng, and L. R. Shah, *J. Phys. Conf. Ser.* **152**, 012038 (2009).
- [7] M. Kapilashrami, J. Xu, K. V. Rao, L. Belova, E. Carlegrim, and M. Fahlman, *J. Phys. Condens. Matter* **22**, 345004 (2010).
- [8] T. Fukumura, Y. Yamada, H. Toyosaki, T. Hasegawa, H. Koinuma, and M. Kawasaki, *Appl. Surf. Sci.* **223**, 62 (2004).
- [9] J. H. Choi, Y. Mao, and J. P. Chang, *Mater. Sci. Eng. R* **72**, 97 (2011).
- [10] R. Waser and M. Aono, *Nature Mater.* **6**, 833 (2007).
- [11] H. Y. Lee, Y. S. Chen, P. S. Chen, T. Y. Wu, F. Chen, C. C. Wang, P. J. Tzeng, M.-J. Tsai, and C. Lien, *IEEE Electron Device Lett.* **31**, 44 (2010).
- [12] C. Walczyk, D. Walczyk, T. Schroeder, T. Bertaud, M. Sowinska, M. Lukosius, M. Fraschke, D. Wolansky, B. Tillack, E. Miranda, and C. Wenger, *IEEE Trans. Electron Devices* **58**, 3124 (2011).
- [13] S. U. Sharath, T. Bertaud, J. Kurian, E. Hildebrandt, C. Walczyk, P. Calka, P. Zaumseil, M. Sowinska, D. Walczyk, A. Gloskovskii, T. Schroeder, and L. Alff, *Appl. Phys. Lett.* **104**, 063502 (2014).
- [14] M. Venkatesan, C. B. Fitzgerald, and J. M. D. Coey, *Nature (London)* **430**, 630 (2004).
- [15] J. M. D. Coey, M. Venkatesan, P. Stamenov, C. B. Fitzgerald, and L. S. Dorneles, *Phys. Rev. B* **72**, 024450 (2005).
- [16] J. M. D. Coey, M. Venkatesan, and C. B. Fitzgerald, *Nat. Mater.* **4**, 173 (2005).
- [17] D. W. Abraham, M. M. Frank, and S. Guha, *Appl. Phys. Lett.* **87**, 252502 (2005).
- [18] N. H. Hong, N. Poirot, and J. Sakai, *Appl. Phys. Lett.* **89**, 042503 (2006).
- [19] N. H. Hong, J. Sakai, N. Poirot, and A. Ruyter, *Appl. Phys. Lett.* **86**, 242505 (2005).
- [20] M. S. R. Rao, D. C. Kundaliya, S. B. Ogale, L. F. Fu, S. J. Welz, N. D. Browning, V. Zaitsev, B. Varughese, C. A. Cardoso, A. Curtin, S. Dhar, S. R. Shinde, T. Venkatesan, S. E. Lofland, and S. A. Schwarz, *Appl. Phys. Lett.* **88**, 142505 (2006).
- [21] M. K. Sharma, D. K. Mishra, S. Ghosh, D. Kanjilal, P. Srivastava, and R. Chatterjee, *J. Appl. Phys.* **110**, 063902 (2011).
- [22] C. Das Pemmaraju and S. Sanvito, *Phys. Rev. Lett.* **94**, 217205 (2005).
- [23] A. Rogalev, J. Goulon, Ch. Goulon-Ginet, and C. Malgrange, in *Magnetism and Synchrotron Radiation of Lecture Notes in Physics*, edited by E. Beaurepaire *et al.* (Springer, New York, 2001), Vol. 565.
- [24] E. Hildebrandt, J. Kurian, and L. Alff, *J. Appl. Phys.* **112**, 114112 (2012).
- [25] E. Hildebrandt, J. Kurian, M. M. Muller, T. Schroeder, H. J. Kleebe, and L. Alff, *Appl. Phys. Lett.* **99**, 112902 (2011).
- [26] E. Hildebrandt, J. Kurian, J. Zimmermann, A. Fleissner, H. von Seggern, and L. Alff, *J. Vac. Sci. Technol. B* **27**, 325 (2009).
- [27] G. H. Chen, Z. F. Hou, X. G. Gong, and Q. Li, *J. Appl. Phys.* **104**, 074101 (2008).
- [28] C.-K. Lee, E. Cho, H.-S. Lee, C. S. Hwang, and S. Han, *Phys. Rev. B* **78**, 012102 (2008).
- [29] A. Winkler, N. Narayanan, D. Mikhailova, K. G. Bramnik, H. Ehrenberg, H. Fuess, G. Vaitheeswaran, V. Kanchana, F. Wilhelm, A. Rogalev, A. Kolchinskaya, and L. Alff, *New J. Phys.* **11**, 073047 (2009).
- [30] K. Nagaoka, A. Jentys, and J. A. Lercher, *J. Catal.* **229**, 185 (2005).