

# Increasing coercivity of ferromagnetic zinc oxide with thermal acetylene treatment

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**Abstract**— We have used a thermal acetylene treatment on ZnO nanorods in order to investigate the possibility of carbon-doping-induced room temperature ferromagnetism in them. The properties of the rods were investigated using SQUID magnetometry and photoelectron spectroscopy and the findings compared to previously reported results. Ferromagnetism was detected in all investigated samples, but no clear correlation between acetylene and the strength of ferromagnetism was observed. A weakening of the hybridization of Zn 3d and O 2p states as a result of acetylene treatment was detected. The coercivity of acetylene-doped samples was observed to be higher than in annealed samples. The findings support the view that ferromagnetism in ZnO is intrinsic in origin and not caused by carbon doping. However, the treatment can still be used to engineer the magnetic properties of the material, as it can tune its surface properties.

## I. INTRODUCTION

Zinc oxide (ZnO) is a versatile semiconductor oxide material with several favourable properties: It has a large band gap of 3.4 eV, and its large excitonic binding energy makes it well suited for different optical applications.[1,2] The ability to synthesize a plethora of different nanomaterials also makes ZnO a very attractive material.[3] A major reason for the contemporary interest in ZnO has been its potential as a dilute magnetic semiconductor (DMS).[4,5] P-type ZnO was predicted to be a DMS with a Curie temperature above 300 K, imperative when pursuing commercially viable spintronic applications.[6] Room-temperature ferromagnetism has been experimentally observed both in transition metal doped ZnO, and later with ZnO doped with carbon, a nonmetallic and nonmagnetic substance.[7–9] Using non-magnetic dopants rules out the possibility of any observed ferromagnetism being due to aggregate ferromagnetic phases of the metal.

Room-temperature ferromagnetism (RTFM) in C-doped ZnO lacks a definitive understanding of the underlying mechanism in spite of several presented theories.[10–13] The observed ferromagnetism has been attributed, for instance, to zinc and oxygen vacancies, oxygen-substituted carbon and bent C-Zn-C units.[14–17] In most cases the magnetic properties have been found to be sensitive to the preparation method.[18] The phenomenon seems to be surface-sensitive, making nanostructures with a large specific surface area good candidates for study.[17] It has even been predicted that the necessary defect concentrations for RTFM in ZnO are unfeasibly large to appear in bulk material, but not so in

surfaces and grain boundaries, meaning that surface-sensitive treatments can have a large effect on ZnO magnetism.[19]

In this paper, we follow on our previous work in introducing carbon to ZnO nanostructures by means of a thermal acetylene treatment.[20] The treatment was originally developed for effectively passivating porous silicon surfaces.[21] The method has proven to be effective in treating TiO<sub>2</sub> nanotubes, and was later modified for use with ZnO, where room-temperature ferromagnetism and major morphological changes were detected.[22,23] A two-step synthesis process can give more versatile tools for engineering, as the steps will not interfere with one another and can be individually optimized to achieve a desired result.

We use a low-temperature chemical process to synthesize ZnO nanorods. This method was chosen for its ease-of-use and potential for industrial upscaling, as little costly equipment is needed and the chemicals used are neither expensive nor very hazardous. The magnetic properties of the ZnO samples were probed using superconductive quantum interference device (SQUID) magnetometry. Normal and resonant (X-ray) photoemission spectroscopy (PES and RPES, respectively) are utilized to probe changes in the electronic structure of the material.

## II. EXPERIMENTAL METHODS

Nano-microsized ZnO rod samples were synthesized on <100> Si wafers (Siegert Wafer, resistivity 0.01–0.02 Ωcm). The samples were made by mixing 0.005 M zinc nitrate and hexamethylenetetramine in an aqueous solution. The method has been described in detail in Ref. [20] and is based on that developed by Vayssieres.[24] Care was taken to avoid magnetic contamination during sample preparation.

The acetylene treatment was done as detailed in Ref. [23]. In a typical experiment, the sample was placed in a quartz tube and flushed with nitrogen gas (1 l/min) for 20 min. Next, a further 1 l/min flow of acetylene gas was added for 14 min 45 s. After cutting the acetylene flow and waiting 15 s in order for excess acetylene to clear the tube, the sample was placed in a furnace at the desired temperature (825 °C) for 10 min. Finally, the tube and the sample were allowed to cool to room temperature while maintaining the N<sub>2</sub> flow. To verify the effect of the treatment, some samples were merely thermally annealed in N<sub>2</sub> flush, using the described process flow without adding acetylene.

SQUID magnetization measurements were recorded using a Quantum Design MPMS (Magnetic Property Measurement System) XL from 10 to 300 K using fields between  $-0.5$  and  $0.5$  T. The electronic structures were measured by a photoemission spectroscopy (PES) system installed at the undulator beam line BL2A in the Photon Factory (PF) at the High Energy Accelerator Organization (KEK) in Tsukuba, Japan. The kinetic energy of the photoelectrons for PES was measured using the Gammadata-Scienta SES-2002 hemispherical analyzer. The energy resolutions of PES was 100 and 60 meV, at  $h\nu = 800$  eV. The energy axis was calibrated by measuring an Au film evaporated onto the manipulator in all the measurements. XPSPEAK 4.1 software was used for fitting.

### III. RESULTS AND DISCUSSION

All studied samples consisted of a white film which darkened after acetylene treatment. The areal density of the nanorod layers was found to be approximately  $5.1$  g/m<sup>2</sup> for untreated rods. By weighing the samples before and after the treatment, we found the acetylene treatment to cause a weight loss of approx. 5 % in the nanorod layer, caused by acetylene eroding the ZnO rods.

Figure 1(a) shows magnetization hysteresis loops from the samples, normalized to sample surface area (which is proportional to sample mass) and measured in 10 K. The data has been smoothed using 5 point adjacent averaging to remove noise from individual points. The substrate contribution and the linear contributions from the sample holder and bulk ZnO have been subtracted. A ferromagnetic signal that saturates below 0.3 T can be observed in all samples. Figure 1(b) shows that hysteresis persists in all samples even in 300 K. It is noticeable that the acetylene-treated sample exhibits strong coercivity in both temperatures.

Figure 2(a) shows the relation between the saturation magnetization and measurement temperature. It can be seen that the N<sub>2</sub>-annealed sample shows little dependence of temperature. The other samples display a drop in saturation magnetization at higher temperatures, but the observation of hysteresis shows that the Curie temperature has not been reached at 300 K for any of the samples. Such temperature independence has previously been observed in similar, doped and undoped ferromagnetic ZnO materials.[17,25–27] No T<sup>-1</sup> type dependence is observed, ruling out superparamagnetism.

The maximum saturation magnetization we observed was of the order  $1$  mA/m<sup>2</sup>, which corresponds to approx.  $2$  mA/m<sup>2</sup>/kg, a value around 10 % of that observed by Kung in [28] and also significantly less than what was seen previously in [23], likely due to differences in the starting material. We consider this a feasible magnitude for intrinsic RTFM.

While previous studies in ([23]) found a correlation between carbon-doping and ferromagnetism, in this study the ferromagnetic saturation magnetization in the acetylene-treated sample is the weakest, though it persists more strongly in higher temperatures than the as-grown sample's, which shows a significant drop already at 200 K. As identical acetylene treatment methods were used in both studies, it is evident that relatively minor differences in the starting

material – chemically grown, nominally pure rod-like wurtzite nanostructures in both cases – can lead to major differences in the properties of the end product.

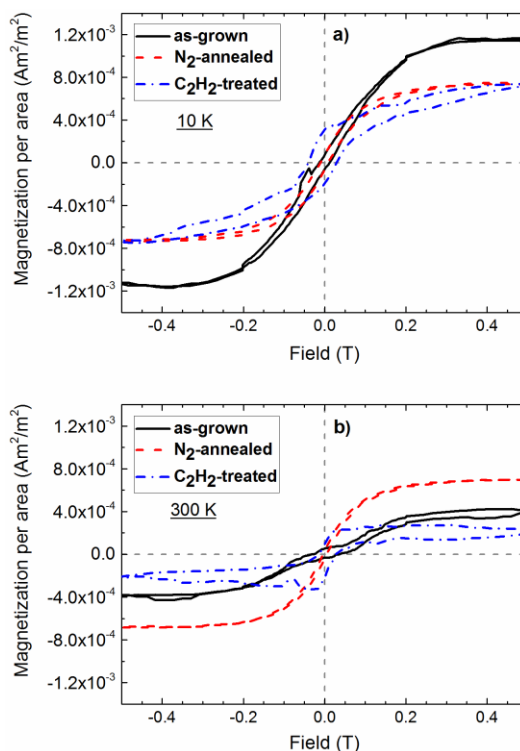


Fig. 1. a) Magnetization loops of the ferromagnetic-like contribution for the samples in 10 K. b) The same loops measured in 300 K.

In Fig. 2(b) the measured coercivity vs. temperature curves from the same samples are shown. At low temperatures, the coercivity in the acetylene-treated sample is significantly higher than in the others, reaching nearly 32 kA/m as opposed to the value of 7 kA/m in the N<sub>2</sub>-annealed sample. The difference vanishes on increasing temperature, with acetylene-treated ZnO consistently retaining a higher coercivity than the annealed sample. The coercivities are somewhat larger than those observed for ZnO films by Xu et al.[29] The coercivity in a material is related to the amount of pinning sites, which in turn is affected by grain size and the amount of defects.[30] Annealing in itself is likely to reduce coercivity by increasing the grain size. The carbon introduced by the acetylene treatment may act as new sites, which would lead to the higher value of coercivity for acetylene-treated samples, especially if ferromagnetism is confined to the surface of the rods. Attaining a high value of coercive force is important for ZnO to be useful in data storage applications, where a reasonably high coercivity is necessary. Further improvement is needed, if the desired coercivity of 350–4000 Oe (28–320 kA/m) above room temperature is to be reliably attained.[31]

The results implicate that ferromagnetism in ZnO is highly sensitive to the properties of the pre-treatment rods. This means that the origin of ferromagnetism is difficult to pin down solely on the carbon induced by the acetylene treatment. In order to create ferromagnetic ZnO materials, the synthesis

process of ZnO itself must be highly reproducible. In [23], the observed ferromagnetism could be attributed to nitrogen-carbon complexes in the rods. However, in our earlier studies on ZnO rods similar to the present case, we detected no nitrogen-related Raman peaks.[20] This means that nitrogen is unlikely to be the root cause of ferromagnetism in the ZnO materials studied here, though it may have contributed to the magnetic phenomena in other reports. Several different mechanisms may promote room-temperature ferromagnetism in ZnO.

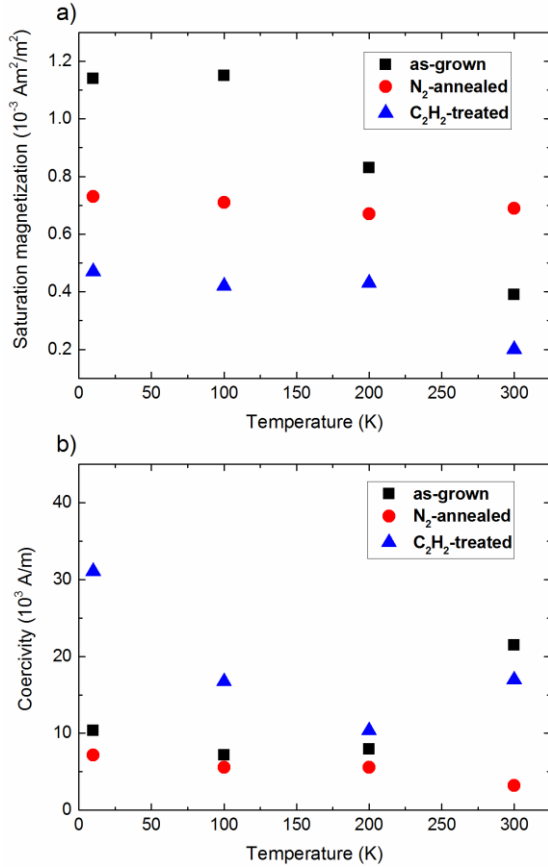


Figure 2. a) Saturation magnetization vs. measurement temperature for ZnO samples. b) Coercivity vs. measurement temperature for ZnO samples.

In PES, the Zn2p peaks were not observed to change between the samples. A standard two-peak fit with nearly Gaussian components was done on the O1s peaks. The fitted values are collected in Table I. Because of surface charging causing an offset to binding energy values, only the relative areas of the component peaks are analyzed. The smaller-energy peak ( $O_A$ ) is attributed to oxygen in the wurtzite lattice, whereas the higher binding energy one ( $O_B$ ) is taken to originate from defective regions of the ZnO lattice.[32] Thus, the ratio of the peak areas can be used as an approximation of the oxide quality in the surface of the rods. This ratio is the largest in the as-grown sample, meaning that oxygen vacancies and other defects are formed in the surface region as a result of heat treatment, similarly to that observed by other reports of annealed ZnO. [33,34] PES only probes the surface,

however, and likely the overall crystal quality of rods grown in low temperatures is relatively poor, as shown by the strong defect-related photoluminescence observed therein.[20,35]

Peak	$O_A$		$O_B$	
	BE (eV)	Area (%)	BE (eV)	Area (%)
As-grown	537.20	34.7	538.14	65.3
$\text{N}_2$ -ann.	537.31	28.5	538.88	71.5
Acet-treat.	537.30	29.9	538.65	70.1

Table I. XPS O1s peak parameters: Binding energy (BE) and relative area (Area).

Fig. 3 shows the resonant PES spectra for all three samples. The intensity of the Zn 3d peak can be seen to decrease both as a result of annealing and even further after acetylene treatment. Such an effect may result from the lessening of Zn in the samples, agreeing with our previous results which hint at the tendency of Zn to evaporate from ZnO when subjected to carbon in high temperatures.[20] However, we do not expect Zn content to drop as a result of mere annealing in nitrogen. The reason for this needs further study.

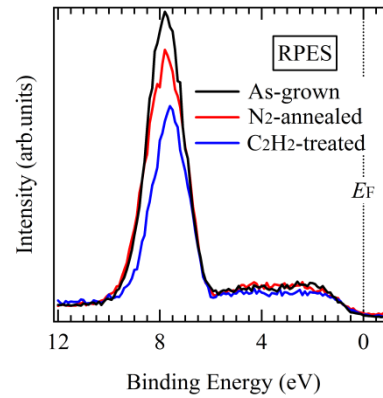


Figure 3. On-resonance RPES spectra from all samples.

The existence of a ferromagnetic signal in samples that have not been acetylene-treated hints at an intrinsic origin, caused by defects. Such defects could include zinc vacancies or their complexes with hydrogen impurities. [36,37]. Oxygen vacancies in the surface of the material have also been proposed in several articles.[38–40] However, we could not detect a correlation between the strength of the RTFM and the amount of oxygen-deficient regions as detected by PES, so it seems unlikely that O vacancies alone could be the cause of ferromagnetism in ZnO.

The outer layer of the rods is a prime candidate for increased densities of ferromagnetism-causing defects, as it consists of smaller nanograins.[20] Such grains would contain a large density of grain boundaries rife for defects to concentrate on. The grain boundary volume is known to be linked to the appearance of RTFM in ZnO.[41,42] Annealing

generally increases grain size and thus lowers the total boundary volume, which would explain why it weakens the saturation magnetism observed here.[43] We suspect that in the present case, acetylene acts by etching some surface ZnO as seen in [20], removing magnetically active ZnO which in turn lowers the saturation magnetization. In the process, some C gets incorporated in the surface, and these C defects act as magnetic pinning sites increasing the coercivity of the material. Further studies are needed to elucidate the role of carbon, but it is clear that C-doping in itself is not sufficient to promote ferromagnetism, and the reason is likely to lie in grain boundaries instead and crystal defects.

#### IV. CONCLUSIONS

An acetylene treatment which has previously been shown to promote ferromagnetism in ZnO was applied on ZnO structures grown with a low-temperature chemical growth method. Room-temperature ferromagnetism was observed in all samples, including those that had been thermally annealed without acetylene, pointing at the intrinsic origin of RTFM. Acetylene was seen to increase the coercivity of the samples. Based on the findings and literature magnetism is thought to originate from the nanoparticle-like surface layer of the ZnO rods and the grain boundaries therein. The effect of acetylene treatment and the magnetic properties of ZnO nanostructures are dependent on the chosen synthesis route, and thus care needs to be taken when choosing methods for engineering favorable magnetic properties in ZnO. Further research is still needed to clarify the exact mechanism behind ferromagnetism.

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