

Coercivity enhancement in V₂O₃/Ni bilayers driven by nanoscale phase coexistence

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We studied the temperature dependence of coercivity and magnetization of V_2O_3/Ni bilayers across the Structural Phase Transition in V_2O_3 . We found a coercivity peak that coincides with the V_2O_3 phase transition on top of an overall increase of the coercivity with decreasing temperature. We propose that this sharp increase arises from a length scale competition between magnetic domains of Ni and phase coexistence during the V_2O_3 phase transition. This model is supported by micromagnetic simulations and shows that magnetic properties of ferromagnetic films are strongly affected by a proximal first order phase transition. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4865587]

Nanoscale manipulation of thin film magnetic properties can be achieved through proximity effects or exchange coupling in bilayer or multilayer structures.^{1,2} The close contact of the layers enables direct insight into the fundamental problems of magnetic and electronic correlations³ and can lead to structures and functionalities with engineered control for technological applications.^{4,5} For example, the proximity of a ferromagnetic film with a vanadium oxide (VO₂ or V₂O₃) results in a reversible modification of the film's magnetic coercivity due to interfacial stress.⁶ This is caused by the magnetoelastic anisotropy adding to the thin film coercivity due to interfacial stress. The origin of the interfacial stress is the Structural Phase Transition (SPT) in vanadium oxides. The SPT coincides with a Metal Insulator Transition (MIT), which is discontinuous and exhibits a phase coexistence with nanoscale domain structure.⁷ V₂O₃ is a prototypical example of such a material, $^{8-11}$ which transitions from a paramagnetic rhombohedral phase in the high temperature metallic state to an antiferromagnetic monoclinic phase in the low temperature insulating state.^{11,12} The V_2O_3 transition is discontinuous and phase coexistence of metallic and insulating phases can be observed.¹³

In this paper, we present the effect of nanoscale phase coexistence during the MIT of V_2O_3 on the magnetic properties of a ferromagnetic Ni thin film. We observe a maximum coercive field and minimum magnetization at temperatures corresponding to the center of the V_2O_3 transition. This maximum is superimposed on the increase in coercivity due to stress within the Ni film. The drastic changes in the magnetic properties are explained by the structural phase coexistence in the center of the V_2O_3 transition. A length scale competition between magnetic domains and phase coexistence in V_2O_3 leads to additional pinning sites within the ferromagnet. Considering the phase coexistence during the phase transition, we present a model and micromagnetic simulations which are in quantitative agreement with the measurements. Our results highlight the importance of relative domain sizes in coupled nanostructured systems.¹⁴ The narrow temperature region in which the maximum change in the magnetic properties is observed may be useful for technological applications. The effects are fully reversible, persistent at each temperature, and show a thermal hysteretic behavior.

V₂O₃/Ni bilayers were prepared in a high-vacuum sputter deposition system with base pressure of 1×10^{-7} Torr. $100 \text{ nm V}_2\text{O}_3$ films were deposited onto (1012) sapphire substrates at 750 °C in 4 mTorr of ultra-high purity (UHP) Ar by RF sputtering at 100 W of a V₂O₃ target. 10 nm thick Ni layers were deposited after cooling to room temperature and recovering the base pressure. A 5nm capping layer of Nb was deposited to prevent oxidization. Ni and Nb were deposited in 4 mTorr of UHP Ar by RF sputtering at 100 W. Temperature dependent structural characterizations were carried out using a Rigaku Smartlab X-ray diffractometer operating between 80K and 300K. Magnetization as a function of field and temperature was recorded using a Quantum Design PPMS-DynaCool Vibrating Sample Magnetometer (VSM) and a Quantum Design superconducting quantum interference device (SQUID) magnetometer, respectively. Electrical transport measurements were performed in a two-probe configuration using a constant current source. The morphology of the thin films at room temperature was investigated with an atomic force microscope (AFM) operating in tapping mode. Since the structural and electronic configuration of the V₂O₃ film crucially depends on the temperature, a slow sweep rate of 1-2 K/min was used in all measurements. Thus, thermal lagging was minimized and reproducible measurements were obtained throughout the V_2O_3 phase transition. Micromagnetic simulations were performed with the Object Oriented Micromagnetic Framework (OOMMF) package from NIST.¹⁵

Fig. 1(a) shows the magnetization as a function of field for selected temperatures throughout the V_2O_3 phase transition. The data have been normalized by the Ni volume and shows symmetric ferromagnetic hysteresis with varying



FIG. 1. (a) In-plane VSM magnetic hysteresis at different temperatures of $V_2O_3(100 \text{ nm})/\text{Ni}(10 \text{ nm})$ throughout the V_2O_3 phase transition. Three measurements above, in the middle, and below the transition are highlighted with enlarged empty symbols. (b) Coercivity and (c) SQUID magnetization (measured at 500 Oe, warming up the sample) as a function of temperature. Note, the maximum in coercive field and minimum in magnetization coincide in temperature.

width. The coercive fields H_C as a function of temperature are summarized in Fig. 1(b). During cooling of the sample, a maximum of $H_C = 211$ Oe was observed at 160 K. This maximum is shifted by about 5 K to higher temperatures for the measurements during heating. This shift is consistent with the thermal hysteresis observed in the V_2O_3 first order transition.⁹ The maximum is asymmetric and the values at lower temperatures remain over a factor of two higher than the values at 200 K. The values of the coercivity below 150 K and above 185 K are independent of the temperature sweep direction. Fig. 1(c) shows the behavior of the magnetization during heating of the sample with a 500 Oe applied magnetic field. A minimum in the magnetization occurs at the same temperature as a maximum in the H_C. The reduced magnetization is observable in Fig. 1(a), with the hysteresis loop at 165 K having the lowest magnetization at 500 Oe. The remanent magnetization is correlated with the coercivity and increases (decreases) as the loop width increases (decreases).

The changes in H_C and magnetization coincide in temperature with the V_2O_3 phase transition, Fig. 2. The MIT observed in the resistance measurements as a function of temperature is shown in Fig. 2(a). Typical V_2O_3 thin films show up to seven orders of magnitude change during the MIT.¹⁰ The resistance values are dominated mostly by the metallic Ni film, the Nb capping layer, and the metallic contact resistance. This leads to the linear behavior and a suppression of the absolute change resulting from the MIT, Fig. 2(a). Nevertheless, a distinct change in resistance is observed between 150 K and 175 K with a thermal hysteresis typical for the V_2O_3 first order transition.

The SPT accompanying the MIT is shown in Fig. 2(b). Each point on the curves corresponds to an individual outof-plane x-ray diffraction measurement at a constant temperature. Above 185 K a single Bragg peak is observed at $2\theta_{\rm R} = 24.35^{\circ}$, corresponding to the (012) plane of the rhombohedral phase of V₂O₃. During the SPT, the high temperature rhombohedral phase transforms into the low temperature monoclinic phase. In the diffraction measurements, this manifests in a Bragg peak observed at $2\theta_{\rm M} = 24.07^{\circ}$, which can be identified with the (110) monoclinic lattice direction.¹² The correct indexing of the high and low temperature diffraction peaks has been confirmed by



FIG. 2. (a) Resistance and (b) crystallographic phase fraction as a function of temperature for $V_2O_3(100 \text{ nm})/\text{Ni}(10 \text{ nm})$.

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measurements along different directions with respect to the surface normal.¹⁶ At each temperature, the data are fitted assuming two Gaussian functions centered at $2\theta_R$ and $2\theta_M$, respectively. These Gaussian fits are integrated and normalized to the highest values obtained for each phase. The measurement is repeated for the heating and cooling temperature branch, leading to the four intensities shown in Fig. 2(b). Both MIT and SPT show a 5K thermal hysteresis in the 180–150 K range. The transition temperatures in the 100 nm films are similar to those observed in bulk V₂O₃. The centers of MIT and SPT are located at the same temperatures at which the maximum coercivity and minimum magnetization are observed.

Increased coercivity below 150 K compared to the values above 190 K was previously observed and attributed to stress in the Ni film.⁶ Above 190 K, the Ni film is in the asgrown relaxed condition and shows lower H_C values. Below 150 K, V₂O₃ has undergone the structural phase transition and the Ni grown on the top is stressed, thus showing higher H_C values. This highlights the direct coupling between the V₂O₃ and Ni films. However, this explanation alone does not account for the maximum of the coercivity observed in the middle of the V_2O_3 phase transition, Fig. 1(b). Additional experiments have shown that a change in coercivity is still present when the V_2O_3 layer is decoupled from the Ni film by a thin Cu spacer layer (data not shown). This indicates that the antiferromagnetic ordering in V₂O₃, if present, is not playing a crucial role in the coercivity enhancement. Furthermore, we have performed measurements in field cooling configurations and all magnetic hysteresis were reproduced without any indication of exchange bias.

We developed a model considering the phase coexistence throughout the first order phase transition and the length scales involved in the coercivity enhancement. We consider crystallographic grains of Ni and V₂O₃ to be of the same size and larger than the lateral domain size of Ni.¹⁷ The crystallographic grain size and the intrinsic Ni magnetic domain size can be considered temperature independent. However, in V₂O₃ both metallic and insulating phases coexist across the transition with varying lateral extension.¹³ Well above the V_2O_3 transition, all magnetic domains in the Ni volume are strain-relaxed and the film has a defined value of coercivity. With decreasing temperature, insulating monoclinic domains nucleate in V₂O₃. Parts of the Ni film, which are in contact with these domains, show a higher coercivity due to stress. The boundary between stressed and unstressed Ni can be considered as a localized structural and magnetic defect. Upon magnetization reversal, this defect acts as a pinning center for magnetic domain wall movement and thus further enhances the coercivity. As the V_2O_3 phase transition progresses, the Ni film becomes more inhomogeneous and reaches a maximum disorder in the center of the transition at which both phases coexist equally, Fig. 2(b). The maximum disorder in the center of the transition produces a maximum in the coercivity, Fig. 1(b). In addition to the increased coercivity, the presence of additional domains reduces the Ni magnetization. This decrease in magnetization within the phase transition is consistent with the experimental observations in Fig. 1(c). Further, cooling of the sample shifts the V_2O_3 phase concentration towards the insulating state and larger monoclinic domains coalesce. As a consequence, the absolute number of pinning sites in the Ni decreases and the coercivity reduces. The final value of the coercivity well below the phase transition temperature corresponds to the stressed Ni film without extra pinning.¹⁸ Coercivity enhancement due to a related phenomenon was observed in STO/Nd_{0.5}Sr_{0.5}CoO₃ films.¹⁹ In this case, the coercivity enhancement is due to an interfacial phase separation leading to additional pining centers.

The lateral extension of magnetic domains and the domain of the SPT is crucial for observation of this behavior. A different lateral disorder, for example, caused by a higher roughness, reduces the magnetic domain size and increases the number of domain walls. Therefore, the initial value of the coercivity above 190 K is expected to be higher. Further, the Ni domains are smaller than the V₂O₃ domains and less additional domain walls are created by the V₂O₃ SPT. Therefore, no peak is observed in the coercivity in the middle of the transition. This behavior can be observed comparing a V_2O_3 /Ni bilayer with 3 nm interface roughness with a sample that has a lower roughness of 1.5 nm, Fig. 3. More importantly, the sample with lower roughness showed terraces of 100 nm width on which the roughness remains below 1 nm, Fig. 3(b). Samples with higher roughness do not show this lateral correlation. For the case of lower roughness, the high temperature values for the coercivity are reduced by more than a factor of two and a clear maximum enhancement is observed, Fig 3(d).

To investigate the hypothesis that nanoscale phase coexistence in V₂O₃ causes magnetic domain separation and domain wall pinning in Ni, we performed a micromagnetic simulation using OOMMF.¹⁵ We model the Ni film with a $1 \,\mu\text{m} \times 1 \,\mu\text{m} \times 10 \,\text{nm}$ Ni slab with an exchange constant of A = 3.4 pJ/m and saturation magnetization $M_8 = 494 \text{ kA/m}$.¹⁷ The slab was discretized into a mesh of $5 \times 5 \times 10$ nm³ cells. For the simulations, we assumed that the Ni and V₂O₃ grains have the same size and the Ni slab is divided into 100 nm $\times 100 \,\mathrm{nm}$ grains according to our AFM measurements, Fig. 3(b). Based on the results shown in Fig. 2, we assumed that the transition temperatures for individual V₂O₃ grains have a mean value of 165 K and follow a Gaussian distribution with a standard deviation of 5 K. Ni domains in contact with a V_2O_3 domain which has undergone the transition are attributed with a randomly oriented anisotropy of $K = 1 \times 10^4 \text{ J/m}^3$.²⁰ The random orientation of the anisotropy is justified considering that Ni is textured only along the outof-plane direction, but is likely to show polycrystallinity in the film plane. This anisotropy breaks the Ni film into $\sim 100 \,\mathrm{nm}$ domains during the magnetization reversal. At the boundary between monoclinic and rhombohedral phases of V_2O_3 we introduce an additional anisotropy due to lattice mismatch of differently strained Ni grains. This lattice mismatch provides the additional domain wall pinning and has been parametrized with an anisotropy of $K = 4 \times 10^4 \text{ J/m}^{3.20}$ The width of the boundary is optimized to 30 nm in order to reproduce Fig. 1(b) quantitatively. Note that the domain wall width parameter $(\delta \approx (A/K)^{1/2})^{17}$ is 18 nm for K = 1 × 10⁴ J/m^3 and A = 3.4 pJ/m, implying that the Ni domain wall width expected from theory is similar to the width of the boundary chosen here. The simulated values of coercivity





FIG. 4. (a) Simulated coercivity and (b) simulated in-plane magnetization as a function of temperature. Note, the maximum in coercive field and minimum in magnetization coincide in temperature.

FIG. 3. (a) and (b) AFM images for V_2O_3/Ni bilayers with different root mean square roughness, (a) 3 nm and (b) 1.5 nm. (c) Vertical profile along the lines indicated in (a) dashed black line and (b) solid red line. (d) Coercivity as a function of temperature for V_2O_3/Ni bilayers with different roughness: 3 nm black triangles and 1.5 nm red squares.

and magnetization as a function of temperature are shown in Fig. 4. At 165 K, a maximum pinning is observed due to largest amount of boundaries. The simulated coercivity reaches a maximum of 180 Oe and the magnetization reaches a minimum, caused by the formation of the magnetic domains. As the cooling continues, all V₂O₃ grains switch to the monoclinic structure, and therefore the boundary becomes smaller and disappears when the phase transition in V₂O₃ ends. In the final state, the phase boundaries and therefore the pinning sites in the Ni film are removed. Only by adjusting the magnitude of the anisotropies and the boundary width, a quantitative agreement between experiment (Fig. 1) and simulation is achieved (Fig. 4). Our simulation does not take into account the general temperature behavior of the Ni film coercivity and magnetization with temperature and thus does not reproduce the evolution of H_C above or below the transition.

In summary, nanoscale phase coexistence of a first order phase transition strongly affects the magnetic properties of a ferromagnetic layer that is in contact. Inhomogeneities and phase coexistence across the V_2O_3 SPT are responsible for a large enhancement in the coercivity and decrease in the magnetization. Both effects occur over the narrow temperature window of the phase transition. A micromagnetic simulation based on magnetic domain wall pinning at phase boundaries agrees with the experimental data. The reversibility and large tunability of the effect make it feasible for technological applications in which nanoscale manipulation is required.

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