Spin Polarization of CrO_2 at and across an Artificial Barrier

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We report a systematic study of the spin polarization of epitaxial CrO_2 films at and across an interface using planar junctions with a superconducting counterelectrode. By chemical modification of the CrO_2 surface before the deposition of the superconductor, junctions with a wide range of barrier strength were obtained. Analysis of the conductance data on these junctions, especially under Zeeman splitting of the superconducting density of states, yields consistent, close to full spin polarization for CrO_2 regardless of the barrier strength.

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With growing interest in devices that utilize the spin degree of freedom of the charge carriers, there is an intensive research effort into materials with high-spin polarization. One class of materials that has attracted particular attention is that of the so-called half metals [1]. In a half metal the two spin species have different density of states (DOS): the Fermi level lies within one spin band while the other spin band has a gap, thus the itinerant charge carriers are 100% spin polarized. The binary oxide CrO_2 is one of the simplest materials that has been predicted [2] to be a half metal. Although large single crystals of CrO_2 are difficult to obtain, production of high-quality epitaxial films have been demonstrated using high-pressure thermal decomposition [3] and chemical vapor deposition (CVD) [4,5], offering tantalizing potential for a variety of spin electronic applications. The most important materials parameter relevant to spintronic device applications is the spin polarization of the conducting charge carriers. For example, the spin polarization of the electrodes directly determines the magnitude of the magnetoresistance (MR) of a magnetic tunnel junction (MTJ). For an MTJ made of half metals, its "off" state would have infinite resistance, resulting in a dramatic enhancement of the magnetotunneling effect at much reduced current density. A material with full spin polarization is also the preferred source for spin injection into semiconductors. Utilizing a spin injector with $p = 100\%$ for a diffusive contact [6] or employing a tunnel barrier [7] would solve the conductivity mismatch problem, a fundamental obstacle for efficient spin injection into a semiconductor from a ferromagnetic metal. It is thus of critical importance to reliably measure the spin polarization of a material, especially at its surface or interface, as in a real device structure.

The spin polarization of CrO_2 films has thus far been measured with superconducting point contact spectroscopy [8,9]. This technique takes advantage of the Andreev reflection (AR) [10] process at a superconductor/normal metal (S/N) interface, which converts the quasiparticle current in the normal metal into the Cooper pair current in the superconductor. In a superconductor/ferromagnet (S/F) contact, Andreev reflection is suppressed due to the spin imbalance in the ferromagnet. Therefore, by measuring the modification to the conductance spectrum one can determine the spin polarization of the ferromagnet. Indeed, spin polarization as high as 96% has been observed in CrO_2 films [9]. This technique is most effective when the S/F contact is in the clean metallic limit where the AR probability is high. When the interfacial barrier strength increases the AR probability quickly decreases and the conduction becomes dominated by quasiparticle tunneling [11], which is not spin resolved when the tunnel barrier is spin independent. In order to use the quasiparticle tunneling to determine the spin polarization of the ferromagnet, one needs to Zeeman-split the DOS of the superconductor. In that case, the contributions from the spin-up and spin-down tunneling current can be separated, resulting in pronounced asymmetrical features in the conductance spectrum. Tedrow and Meservey [12] were the first to use this asymmetry to calculate the spin polarization of ferromagnetic metals in planar tunnel junctions. The Zeeman splitting is generally accomplished by the application of an external magnetic field, hence it is required that the superconductor have a large enough critical field (>2 T) and small spin-orbit coupling. Since most conventional superconductors have low critical fields in bulk form due to the orbital depairing of the magnetic field, the high critical fields can be realized only by using ultrathin films and having the magnetic field parallel to the film plane to minimize the orbital effects. These conditions are not possible to realize in the point contact method. Therefore, although the point contact technique is a convenient and flexible tool for measuring the spin polarization in metallic contacts, it loses its effectiveness as the barrier strength increases and the junctions approach the tunneling regime. Unfortunately, this is the regime where most of the application interest lies. Furthermore, it has been demonstrated that the spin polarization of a material at surface may be drastically altered from its bulk value in magnitude and even in sign, depending on the nature of the interface [13].

CrO_2 is a metastable phase requiring high pressure and temperature to produce in bulk powder form. The surface of CrO_2 begins to degrade into the more stable Cr_2O_3

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phase (an antiferromagnetic insulator), and possibly other Cr oxides, almost immediately after growth. The thickness of this surface layer increases with time. Ji *et al.* [9] observed a precipitous drop in the measured spin polarization of CrO_2 as the (native) barrier strength increases. The authors attributed this decline to increased (inelastic) scattering as the native barrier becomes thicker over time, which might explain why Co-CrO_2 MTJs using this natural barrier showed an MR much smaller than expected [14]. It is therefore important to explore barriers that will preserve the high bulk spin polarization of CrO_2 and to develop a versatile method to measure the spin polarization at the interface under varying barrier strength.

In this Letter, we have developed a method in which the surface of CrO_2 is chemically treated in order to obtain a consistent and reproducible barrier, allowing systematic measurement of the spin polarization of CrO_2 using planar junctions with superconducting counterelectrodes (Pb and Al). These $CrO_2/I/S$ junctions serve as a model system for the development of a procedure to determine the spin polarization at a wide range of barrier strengths from metallic contact to tunnel junctions.

The CrO_2 films used in this study were grown with a CVD method described in detail elsewhere [15]. Al_2O_3 (0001), TiO_2 (110), and TiO_2 (100) were used as substrates, resulting in polycrystalline, epitaxial (110) and (100) CrO_2 films, respectively [16]. While similar results were observed for Pb junctions on all substrates, Al junctions were fabricated on TiO_2 (110) because of the smooth film surface and ease of etching. The films were patterned into stripes, ~0.5 mm wide, either by post growth lithography and wet etching or by selective growth on a prepatterned SiO_2 template [17]. The stripes were then etched in a Br/methanol solution (12–20 vol % Br) for 120 sec to create a controlled insulating layer on the surface of CrO_2. The samples were then immediately loaded into a vacuum system for the deposition of the counterelectrode.

Examination of the surface of Br etched CrO_2 films with ESCA indicated no trace of Br or organic materials and revealed an O/Cr ratio of 1.6, consistent with a Cr_2O_3 surface layer. This implies that the Br etch is not a simple chemical etching. By controlling the concentration and time of the Br etch we were able to produce junctions of different barrier strength and a wide range of junction resistances. We have studied more than two dozen junctions covering resistances from 10^{-1} to 10^6 Ω. The quality of such barriers was seen, via transport, to decay with time when they were left in either vacuum or air before deposition of the counterelectrodes. Both Pb and Al counterelectrodes were used in this study: the Pb was deposited by thermal evaporation, while the Al was sputtered with dc magnetron. The $CrO_2/I/Al$ junctions were used in the Zeeman splitting experiments because of the high parallel critical field in thin Al films. The conductance spectra were obtained in a ^{3}He system using standard phase sensitive lock-in detection.

Figure 1a shows the conductance spectrum of a $CrO_2/I/Pb$ junction taken at 400 mK in zero magnetic field. The data fit well to the superconducting DOS, and the Pb phonon structures are clearly observed, indicating that this is a high quality tunnel junction where the conduction across the barrier is dominated by elastic tunneling. Although the zero-field conductance data from such a tunnel junction cannot be used to elucidate the spin polarization in the ferromagnet, the results are significant in that they showed an absence of observable inelastic scattering in the barrier thus created. In contrast, Fig. 1b shows the conductance of a highly transmissive CrO_2/Pb junction, fabricated without the Br-etch step, in zero field at 1.2 K, where AR is the main conduction mechanism. Here the conductance peaks at $\pm\Delta$ have disappeared because AR does not require available quasiparticle states in the superconductor. The subgap conductance is suppressed instead of enhanced due to the deficiency of minority spins available for Cooper paring. The data are fit to a modified [8,9,18] theory of Blonder, Tinkham, and Klapwijk (BTK) [11] which takes into account the spin imbalance in the ferromagnet. There are two fitting parameters: the spin polarization p of the ferromagnet and a dimensionless parameter Z that measures the barrier

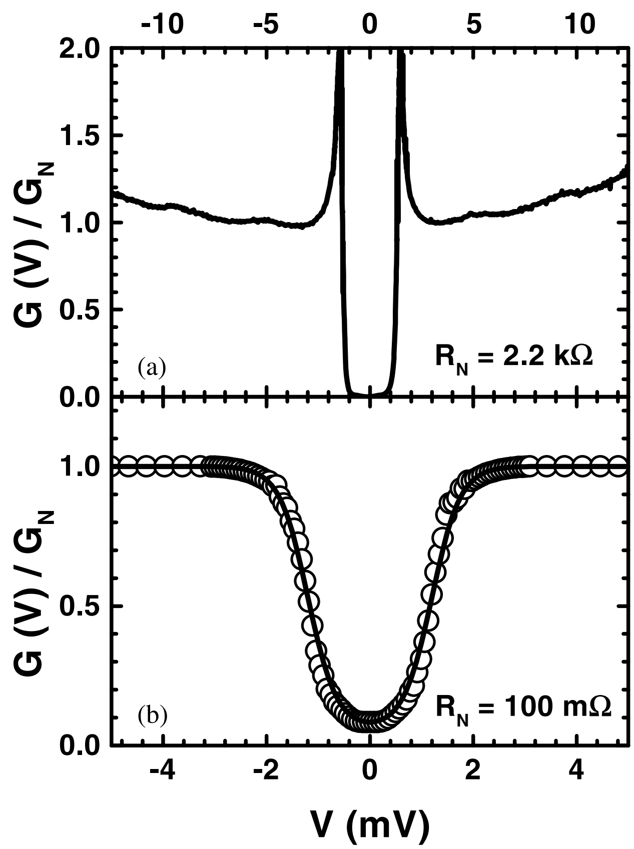

FIG. 1. (a) Normalized conductance data of a $CrO_2/I/Pb$ tunnel junction taken at 400 mK and zero applied field; (b) Normalized conductance data of a CrO_2/Pb junction (open circles) taken at 1.2 K and the best fit to a modified BTK theory (solid line), with $Z = 0$ and a spin polarization of 97%.

strength [11]. For this junction we obtained $p = 97\%$ and $Z = 0$, indicating a high spin polarization for the CrO_2 film and a transmissive metallic contact.

Figure 2 shows the normalized conductance of two $CrO_2/I/Al$ junctions with different barrier strengths. In comparison to the two conductance curves shown in Fig. 1, these two junctions lie in between the two extremes of tunnel junction and metallic contact. There are now moderate conductance peaks at $\pm\Delta$ and the zero-bias conductance is finite. In these junctions the transport across the barrier is a mixture of AR and tunneling. Fitting the data to the modified BTK theory yields Z values of 2.68 (Fig. 2a) and 1.84 (Fig. 2c). Most importantly, despite the high Z values, we obtained $p = 94\%$ and 90%, respectively, from the fits, implying that the strong interfacial scattering at this type of barrier does not affect the spin polarization of the current. To be more specific, the high degree of spin polarization of bulk CrO_2 is preserved at this CrO_2/barrier interface and the spin injection efficiency across this barrier is close to 100%.

At high Z values the AR probability declines quickly [11] and the transport across the junction becomes dominated by tunneling. In a N/I/S tunnel junction, any inelastic processes in the barrier or in the superconductor cause deviation from the expected DOS [19]. The inelastic scattering broadens and reduces the height of the conductance peaks at $\pm\Delta$ and increases the zero-bias conductance; these are qualitative changes that may resemble the effects of spin polarization in a high-Z F/I/S contact. The inelastic effects in a tunnel junction were treated phenomenologically by Dynes *et al.* [19] with the inclusion of a broadening factor, Γ, in the superconducting DOS. Figures 2b and 2d show the best fit to the data using this formalism, yielding $\Gamma = 2$ and 35 μeV, respectively. Clearly, the modified BTK theory based on AR produces a better fit to the data. Nevertheless, the closeness of the two types of fits in Fig. 2 implies that the interpretation of data from high-Z junctions requires extra caution and the extraction of p from the zero-field conductance becomes increasingly unreliable as Z increases. As an example of this potential danger, we have generated two conductance curves (shown in Fig. 3), one based on modified BTK theory ($p = 45\%, Z = 4.00$) and one from inelastic lifetime effects ($\Gamma = 1.5$ μeV). The two curves are indistinguishable.

In order to extract p reliably for high-Z junctions beyond ambiguity, it becomes necessary to Zeeman-split the superconducting DOS so that the conductance from the spin-up and spin-down channels can be separated and compared. The procedure to extract p from the field-split conductance in tunnel junctions has been developed to sophistication [20,21] and now includes the small effects of orbital depairing and spin-orbit coupling in Al. In Andreev contacts with finite, nonzero Z, both AR and tunneling contribute to transport. Since the Andreev conductance and the tunneling conductance are split in different ways under a magnetic field [22], the resulting conductance curve for junctions with intermediate Z is expected to be complex and unique, providing an independent unambiguous alternative method to measure and verify the spin polarization. In principle, a complete

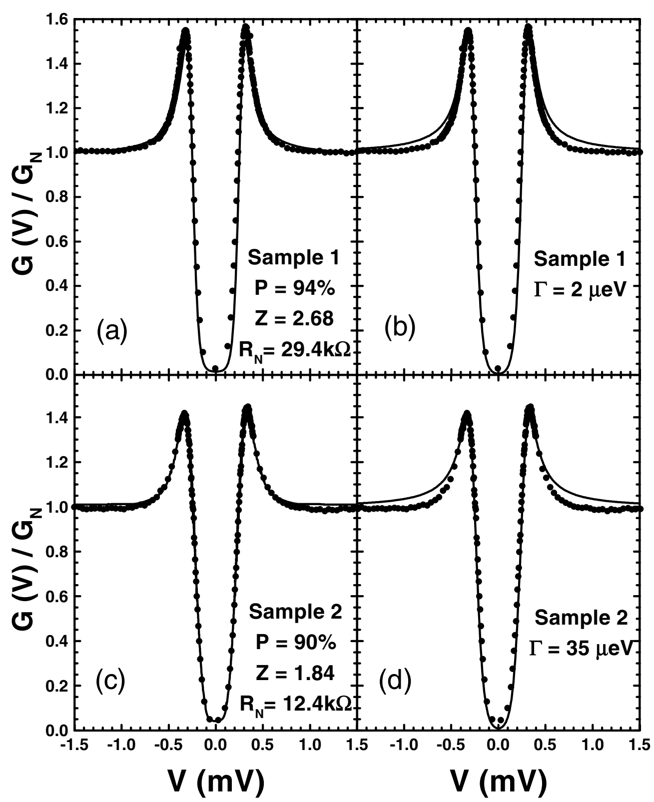

FIG. 2. Conductance data (closed circles) for two $CrO_2/I/Al$ samples taken at 400 mK with fits to both the modified BTK [(a) and (c)] and inelastic broadening models [(b) and (d)]. The modified BTK model yields better fits and indicates high-spin polarization for high-Z junctions.

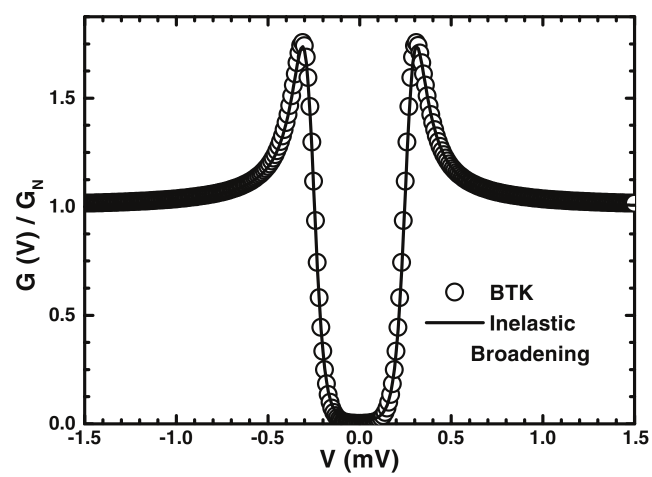

FIG. 3. Two generated conductance curves ($\Delta = 300$ μeV, T = 400 mK) based on the modified BTK (open circles, $Z = 4.0$, $P = 45\%$) and the inelastic broadening (solid line, $\Gamma = 1.5$ μeV) theories. The two curves are indistinguishable in this high-Z region.

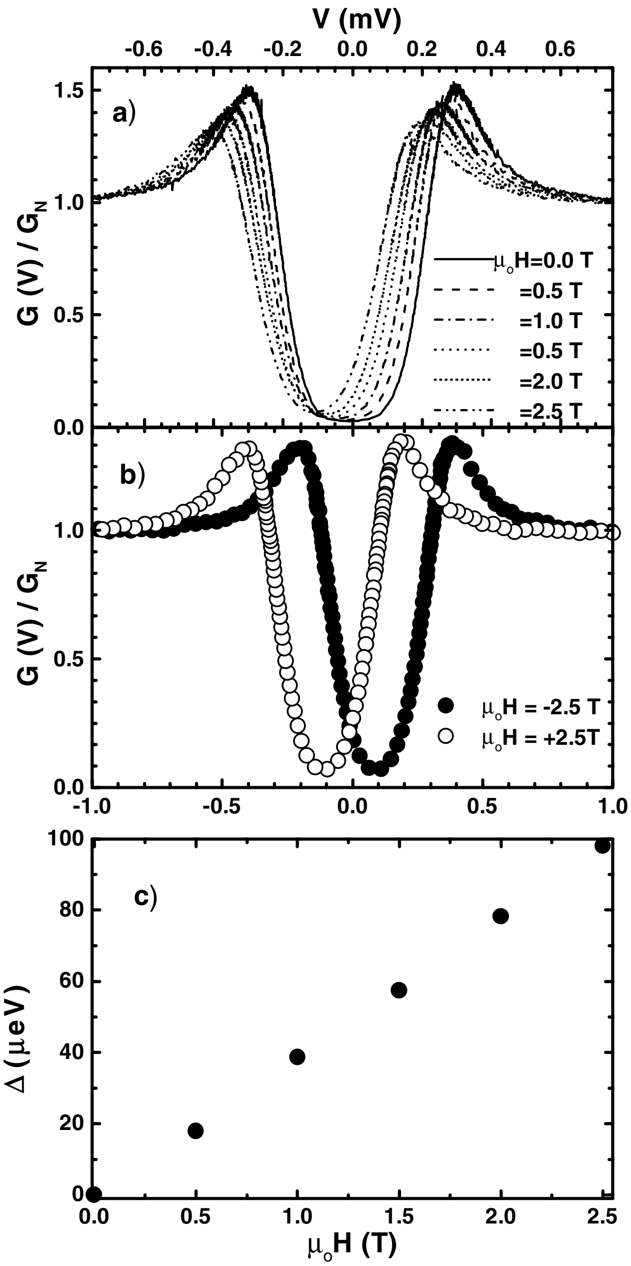

FIG. 4. (a) Zeeman-split conductance curves of a $CrO_2/I/Al$ junction taken at 400 mK ($R_N = 9.3$ kΩ) with applied fields ranging from 0 to 2.5 T in increments of 0.5 T; (b) Data of the same sample at ± 2.5 T. The curves are symmetric in field and exhibit no features attributed to minority spins; (c) The linear shift of the gap edge as a function of field.

formalism similar to that for tunnel junctions [20,21] is needed to analyze the conductance and extract p. However, in the case the ferromagnet is a half metal the picture is qualitatively simple: the magnetic field is expected to induce a mere parallel shift of the conductance curve and no signatures corresponding to the presence of minority spins should emerge. In Fig. 4a we show the conductance curves of yet another high-Z $CrO_2/I/Al$ junction ($Z = 2.76$, $p = 92\%$ from modified BTK fit) at various parallel magnetic fields. Here the Al had a thickness of 90 Å yielding a critical field of 3.4 T. Clearly, the data exhibit a systematic linear (Fig. 4c) parallel shift of the conductance curve from that in zero field. As shown specifically in Fig. 4b, there are no observable additional features due to the minority spins in fields as high as 2.5 T. This is unambiguous evidence that we have achieved close to fully spin polarized current across the $CrO_2/I/S$ junctions even at high-barrier strength. Therefore, we show that the high-spin polarization in bulk CrO_2 can be preserved at and across an artificially modified barrier. This type of barrier is potentially useful for constructing high-MR MTJs based on CrO_2.

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