Effect of Ar ion irradiation on the room temperature ferromagnetism of undoped and Cu-doped rutile TiO_2 single crystals*

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Remarkable room-temperature ferromagnetism was observed both in undoped and Cu-doped rutile TiO_2 single crystals (SCs). To tune their magnetism, Ar ion irradiation was quantitatively performed on the two crystals in which the saturation magnetizations for the samples were enhanced distinctively. The post-irradiation led to a spongelike layer in the near surface of the Cu-doped TiO_2. Meanwhile, a new CuO-like species present in the sample was found to be dissolved after the post-irradiation. Analyzing the magnetization data unambiguously reveals that the experimentally observed ferromagnetism is related to the intrinsic defects rather than the exotic Cu ions, while these ions are directly involved in boosting the absorption in the visible region.

Keywords: single-crystal TiO_2, Cu ion implantation, Ar ion irradiation/post-irradiation, room-temperature ferromagnetism

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1. Introduction

Following the first observation of room temperature ferromagnetism (RTFM) in Co-doped TiO_2,[1] TiO_2-based diluted magnetic semiconductors (DMSs), in which a small quantity of transition-metal ions are randomly introduced into Ti sites of the semiconducting host lattice, have attracted substantial attention due to the superior properties that such materials possess,[2,3] in particular with regard to their potential use in spintronics devices that can accommodate both charge and spin of electrons in a single substance.[4] Until now, throughout most of the published papers, the ever important question of how to precisely determine the nature of defects responsible for the experimentally observed RTFM remains open,[5–7] especially for the systems doped with magnetic elements, i.e., Fe, Co, Ni, probably forming metallic clusters.[5,8] Cu and its oxides are not ferromagnetic, so that makes it an ideal dopant for exploring the origin of FM in TiO_2 based DMSs. Even though such cases are rarely studied from an experimental point of view, FM ordering in these systems is still debated whether the substituted Cu ions can favor the FM.[9–12] On the other hand, Coey *et al.*[13,14] have introduced a new concept so-called d^0 magnetism, according to which the RTFM observed in undoped TiO_2[15,16] is mediated by oxygen vacancies (V_O) that can form bound magnetic polarons (BMPs).[17] Actually, V_O are easily created in n-type TiO_2 samples, making it more difficult to elucidate the mechanism.

In this paper, to avoid any extrinsic FM signals and also to evaluate the doping effect on the FM, we thereby extended the study to Cu-doped TiO_2 single crystals by means of the ion implantation technique for its advantages.[18] Ar ion irradiation, whose irradiation damage effect was calculated to be similar to that of the implantation, was also carried out to run as a proper control. Furthermore, the post-irradiation aiming at decreasing the number of the substituted Cu ions and at further generating defects was also performed on the Cu-doped TiO_2 SC to clarify the issue.

2. Experiment

Commercial pure rutile TiO_2 (001) SCs with one side polished from MaTeck were cut into 10.0 mm×10.0 mm×0.5 mm. The 80 keV Cu ions were implanted into the polished side of each SC with a fluence of 1×10^{16} ions/cm^2, resulting in a projected range of 37.8 nm with a longitudinal straggle of $\Delta R_p = 15$ nm as calculated by the stopping and range of ions in matter (SRIM) code. The energy and dose of Ar ion irradiation/post-irradiation were accordingly estimated to be 55 keV and 2×10^{16} ions/cm^2 via the SRIM. As a consequence, the four samples, pure, as-irradiated, as-implanted, and as-post-irradiated TiO_2 SCs, are respectively labeled as samples 1, 2, 3, and 4. After the

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irradiation/post-irradiation, SQUID magnetometry, transmission electron microscopy (TEM), Doppler broadening energy spectra (DBES, from ∼0 to 20 keV), micro-Raman spectra (325 nm), x-ray diffraction (XRD, Cu K_α) and ultraviolet–visible (UV–vis) diffuse reflectance spectra were employed to characterize the magnetic, microstructural, and optical properties of the samples. All the above measurements were performed at room temperature (RT).

3. Results and discussion

Figure 1 depicts the raw magnetic data of the four TiO_2 SCs. All samples exhibit clear FM behavior, even including the pure SC. An essential point here to emphasize is that any contamination, except some uncontrollable adsorbed carbon species, that could give rise to FM should be ruled out, as in each case no trace of any magnetic elements was detected (by XPS and EDX, not shown here). For TiO_2, neither the native Ti^{4+} and O^{2-} nor the reduced Ti^{3+} is magnetic. Since TiO_2 is naturally an n-type semiconductor due to its deviation from stoichiometry, the unique observed RTFM is more appropriate to be associated with the formed BMPs in which one intrinsic V_O by capturing an electron with an oppositely directed spin between the coupling Ti^{3+} ions favors the FM.[16] We further investigated the FM in the pure SC by annealing it at 1000 °C for 120 min in air to suppress the number of V_O, which turned out to be reasonably in accordance with the BMP model. Contrary to what was observed in the annealed SC, with the increase in V_O, the saturation magnetizations (M_S) of the other SCs are slightly increased, especially in the case of sample 4. At this point, it is interesting to note that the M_S of sample 2 is nearly equal to the value of sample 3 when they were treated in similar damage conditions regardless of whether the ions were Ar or Cu. However, compared with the pure one, the M_S of sample 2 or 3 seems not so sensitive to the improved concentration of V_O, which may support the idea that FM is essentially derived from the BMPs.

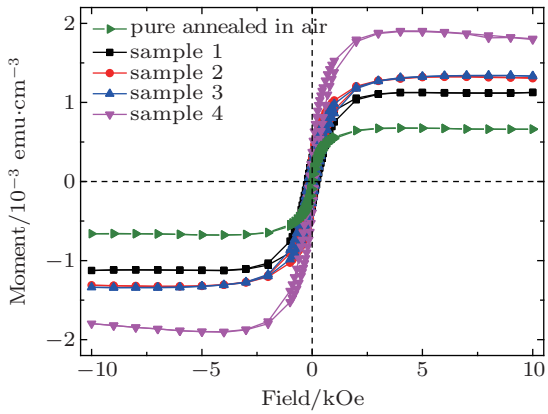


Fig. 1. (color online) *M–H* curves of the four samples and *M–H* curve for the pure TiO_2 SC annealed at 1000 °C in air for 120 min.

Cross-sectional TEM bright-field micrographs of the four SCs are displayed in Fig. 2. TEM image taken from the pure SC in the vicinity of the surface in Fig. 2(a) is also present here for comparison. Figures 2(b) and 2(c) illustrate the SCs irradiated with Ar and implanted with Cu ions. Clearly, their morphological features suggest that the two samples have a similar depth profile. This indicates that the magnetic data of the two samples are comparable by consideration based on the magnetic properties of the two kinds of ions. As seen in Fig. 2(d), a spongelike layer reaching a thickness of ∼ 47 nm emerged after the post-irradiation. Ar ions would be trapped in the induced defects and then got charged when injected into the implanted SC. Those ones near the surface would be escaping from the bulk, leaving behind numerous microvoids, whereas, instead of running away, the implanted Cu ions just bonded to the local and gradually formed nanoparticles or clusters in the deposited layer of about 120 nm thick. Therefore it can be concluded that the spongelike layer was induced by the escape of Ar ions and that an amorphization transformation occurred in this layer. There are other related spectral features that are worthwhile mentioning in this layer, that is, any discernable sign of Cu precipitates could not be easily found anymore and V_O increased sharply due to the presence of the microvoids. Note that if the substituted Cu ions necessarily contributed to the FM, the obtained M_S of sample 3 would be the highest. In fact, however, as shown in Fig. 1, the M_S of sample 4 is incompatible with that viewpoint but the BMPs. Consequently, we hereby propose that RTFM in TiO_2 SCs is mediated by V_O rather than the substituted ions.

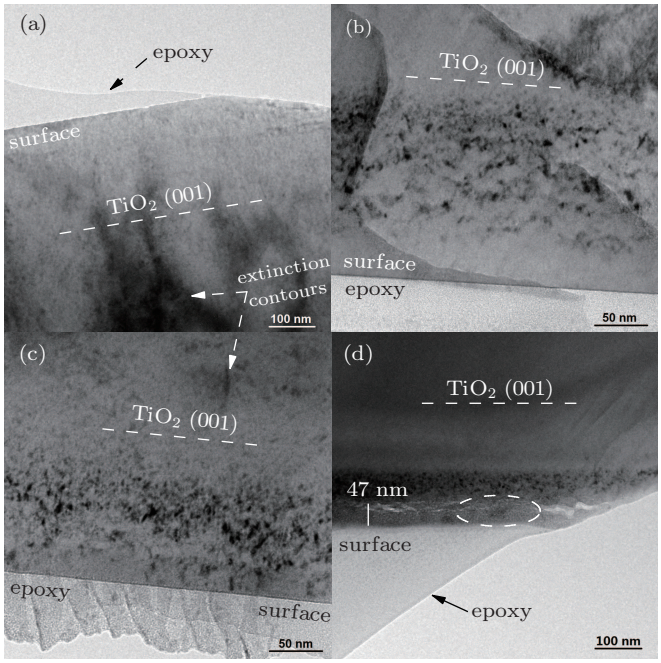


Fig. 2. Typical TEM cross-sectional images taken from (a) pure TiO_2 SC, (b) Ar ion irradiated TiO_2 SC, (c) Cu ion implanted TiO_2 SC, and (d) Ar ion post-irradiated Cu-doped TiO_2 SC. The encircled portion denotes the spongelike layer.

The depth profile of each sample was accurately probed by the DBES to investigate the damage distributions of the four SCs.[19] The mean positron-implantation depth governed by the beam energy was converted through a simple empirical relation.[20] Figure 3 exhibits the plots of *S*-parameter versus the mean positron implantation depth. The *S*-parameter, which represents the fraction of positrons annihilating with the low momentum electrons, reflects a high degree of nonstoichiometry in the near surface of the pure SC.[21] For samples 2 and 3, the line shapes agree well with each other in the depth below 33 nm, indicating that the induced defect concentrations follow a similar depth distribution to the implant profiles. Apparently, it is quite reasonable for sample 4 to assign the higher *S*-parameter to the increased defects due to the post-irradiation in the range of approximately 33 nm to 120 nm where the defects are nicely defined. Without taking into account the surface layer of 33 nm thick, the *S*-parameter behavior of the four samples in some sense is consistent with the results from the *M*–*H* curves. An *S*–*W* map can be utilized to assess the presence and type of defects detected in different layers.[19] The corresponding *S*–*W* maps are shown in the insets. All points of each sample form a straight line and the four lines are almost overlapped (not shown here), therefore suggesting that positrons were trapped in vacancies of the same type. In view of this, it appears that the doping effect is just to boost the number of defects.

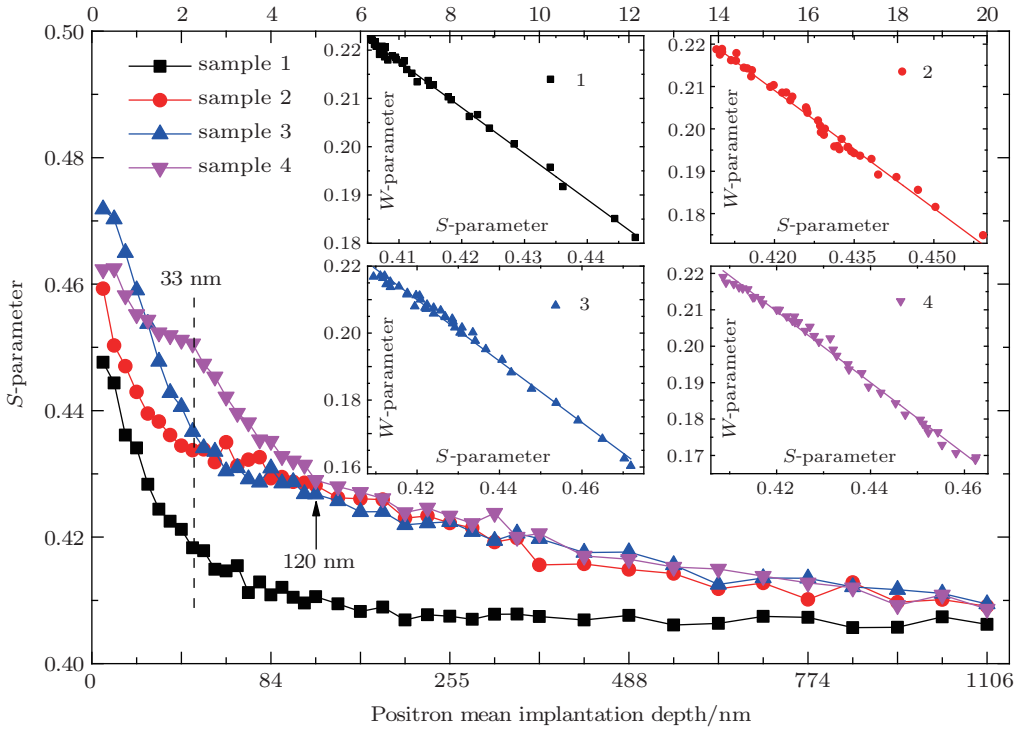


Fig. 3. (color online) DBES measurements of the defined *S*-parameter as a function of the mean positron implantation depth. The upper horizontal axis shows the corresponding positron implantation energy. Insets are the corresponding *S*–*W* maps.

The structural evolution upon the SCs was determined by Raman spectra. The Raman spectra collected from the four samples in the range of 50–1000 cm^{-1} are displayed in Fig. 4. Interestingly, besides the four rutile TiO_2 vibrational bands (B_{1g}, E_g, A_{1g}, and B_{2g}),[22] a sharp peak and a shoulder with a broad peak emerge and can be respectively ascribed to a surface vibrational mode (SV), and to second-order scattering (SO).[23,24] It seems that the irradiation or implantation did not bring about any pronounced changes other than the broadening and shouldering of the peaks. If we consider the linewidth of A_{1g} mode at ~ 611 cm^{-1}, namely, 43.71 cm^{-1}, 67.43 cm^{-1}, 63.72 cm^{-1}, and 123.75 cm^{-1}, as a signature of the loss of crystalline long-range ordering, it is indeed plausible that the radiation damage originating from Ar or Cu ions is highly reflected in the Raman spectra. The variation in the linewidth notably aligns with what has been discerned in the DBES and also with the M_S results described above.

Figure 5 represents the normalized XRD patterns close to the rutile TiO_2 (002) peak. Shoulders outlined by a dashed circle on the left side of the main peak can be clearly identified. These shoulders can be taken as a strong indication of a lattice expansion in each sample.[25,26] In an n-type TiO_2 semiconductor, Ti^{4+} ions (0.605 Å) in octahedral coordination tend to be reduced to Ti^{3+} (0.670 Å) to keep the charge balance when neighbor V_O are created. Hence, the shoulder presented in sample 1 should be due to the presence of the reduced Ti^{3+} ions, revealing a substoichiometric nature of the pure SC. According to the BMP model, Ti^{3+} ions are essential to form

BMPs that allow for long-range FM, so this shoulder is sufficient to explain the significant intrinsic M_S in the pristine SC. Additionally, a new peak corresponding to a CuO-like phase detected in the Cu-implanted SC was found to be dissolved after the post-irradiation.

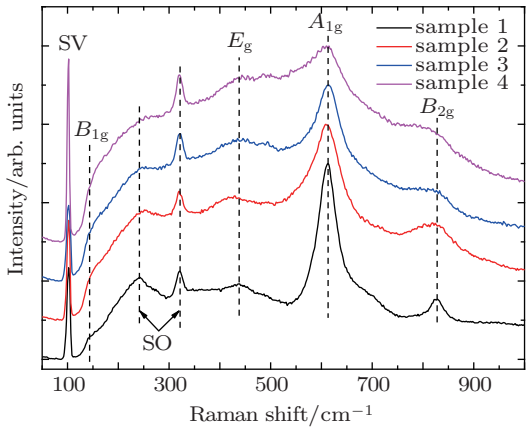


Fig. 4. (color online) Micro-Raman spectra of the four SCs. Note that all curves shown here were normalized for comparison.

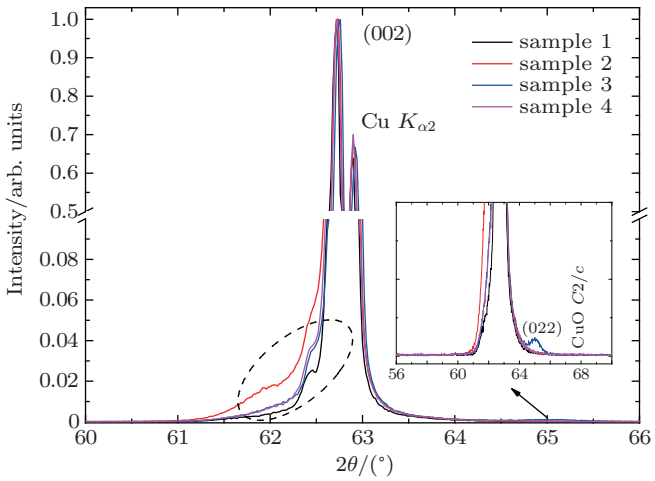


Fig. 5. (color online) Normalized XRD patterns of the four SCs. The dashed circle indicates the present shoulders. Inset shows an expanded view.

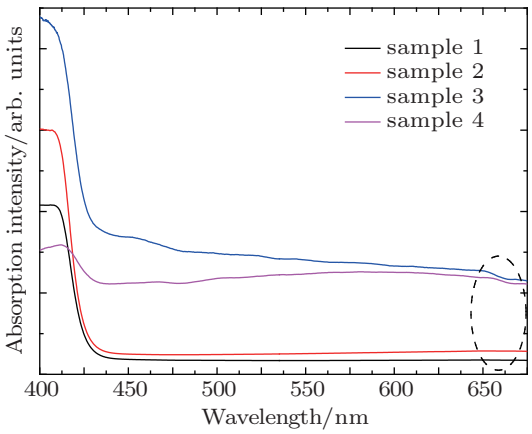


Fig. 6. (color online) UV–vis absorption spectra of the four SCs. The encircled portion denotes a new absorption band at around 660 nm.

The UV–vis spectra of the four SCs obtained in the diffuse reflectance mode are presented in Fig. 6. From the analysis of XRD, we confirmed a new phase of CuO-like species in general having a characteristic band gap of about 1.9 eV,[27] corresponding to the case at $\sim$ 660 nm marked by the dashed circle. By contrast, there appears to be a strong absorption band over the visible range in samples 3 and 4 owing to the substitution of Cu ions in the Ti^{4+} sites.[28] However, as seen, the intensity of the band decreased after the post-irradiation, signifying that some substituted Cu ions are absent from the host lattice. In this sense, the evidence is now accumulating that the observed FM is intrinsic and essentially independent of the substituted Cu ions.

4. Conclusion

In summary, RTFM was observed in the four rutile TiO_2 SCs and is actually dependent on the concentration of defects, namely, V_O. Any possible contributions from the impurities to the M_S were excluded. In contrast to the M_S of the irradiated SC, a Cu-implanted one behaved similarly. Moreover, the M_S of the implanted SC was found to be increased after the post-irradiation, contrary to the result from the annealed SC, which reveals that FM in the SCs was mediated by the formed BMPs rather than any substitutional effect. To further understand the influence of the intrinsic defects on the magnetic response, additional work on the annealing effect is now under progress.

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