Vacancy identification in Co$^+$ doped rutile TiO$_2$ crystal with positron annihilation spectroscopy

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Abstract. Co-doped rutile TiO$_2$ films were synthesized by ion implantation. Variable energy positron annihilation Doppler broadening spectroscopy and coincidence Doppler broadening measurements were performed for identification of the vacancies. A newly formed type of vacancy can be concluded by the S-W plot and the CDB results indicated that the oxygen vacancy (V$_O$) complex Ti-Co-V$_O$ and/or Ti-V$_O$ are formed with Co ions implantation and the vacancy concentration is increased with increase of dopant dose.

1. Introduction

Since the observation of room temperature ferromagnetism (RT-FM) in cobalt doped TiO$_2$ crystal, the diluted magnetic semiconductors (DMS) have led to intense interest in these materials due to their potential use in spintronic devices, which make use of both the spin and charge of electrons$^{[1-5]}$. The origin of ferromagnetism is nowadays a hot topic and is not clearly understood$^{[1-8]}$. The strong interaction between Co ions and O vacancy was found to play a key role in the occurrence and stability of FM$^{[3, 9-12]}$. Calculations indicated that Ti$^{3+}$ ions with one 3$d$ electrons are usually generated in slightly reduced TiO$_2$$^{[12, 13]}$. However, experimental identification of the oxygen vacancy complex has remained unresolved. There is thus a great need to experimentally clarify the oxygen vacancy complex.

Positron annihilation spectroscopy (PAS) is a powerful technique for evaluating vacancy-type defects$^{[14-18]}$. Thermalized positrons in solids get trapped at vacancies because of the missed positive charge of the ion cores and finally annihilated with surrounding electrons. At vacancies, positron-electron momentum distribution is narrowed due to the reduced electron density. Meanwhile, the core electron momentum distribution can be used to identify the atoms around the vacancies. Coincidence detection of broadened annihilation photons (CDB) can eliminate random background and yield three orders of magnitude better signal-to-noise ratio in Doppler broadening measurements, which enables us to observe the high-momentum annihilations with core electrons specific to each element$^{[19-21]}$. Thus, CDB measurements are expected to provide additional information about the atoms surrounding...
the annihilation site. For this end, we prepared a series of Co⁺ ion implanted rutile TiO₂ and characterized the vacancies inside them by PAS method.

2. Experimental

Five rutile TiO₂ (110) crystals with thickness of 500 um were purchased from Shanghai institute of optics and fine mechanics, Chinese academy of sciences (CAS). Samples 1# to 4# were implanted with the dose of 1.25×10¹⁶ ions/cm², 2×10¹⁶ ions/cm², 3×10¹⁶ ions/cm² and 4×10¹⁶ ions/cm² at institute of semiconductors, CAS. The implanting energy was fixed to be 100 keV for all samples with the mean implanting depth about 40nm which can be simulated by SRIM code. Also an un-doped sample marked 0# was prepared for comparison.

The Doppler broadening annihilation radiation at 511keV peak was recorded by a HPGe detector. The line width is characterized by S and W parameters. The S parameter is defined as the ratio of the gamma-ray counts in the central part of the 511 keV peak (510.24–511.76 keV) to that in the entire peak (504.2–517.8 keV). W parameter was defined as the ratio of the summed gamma-ray counts in the range of 513.6–517.8 keV and 504.2–508.4 keV to the total number of counts in the entire peak.

For CDB measurement, the energies of annihilating γ ray pairs (denoted by E₁ and E₂) are simultaneously registered in the two detectors located at nearly 180° to each other. The difference of the energies of the two γ rays is given by cPL and the total energy E₇=E₁+E₂ is given by 2m₀c² (neglecting the thermal energies and chemical potentials), where PL is the longitudinal momentum component of the positron-electron pair along the direction of the γ ray emission, c is the speed of light and m₀ is the electron rest mass. Selecting the coincidence event under the condition of 2m₀c²−2.4keV<E₇<2m₀c²+2.4keV, each spectrum is collected for more than 38 hours to get eight million counts. The single-detector Doppler broadening and CDB measurements were performed at Beijing intense slow positron beam.

3. Results and Discussion

Fig.1 S parameters as a function of incident positron energy. Fig. 2 S-W plot of all samples.

The S parameters of all samples as a function of positron incident energy from zero to 10 keV are shown in figure 1. The S parameters decreased gradually from sample surface until deep inside the bulk. When Co⁺ was implanted, the S parameter decreased sharply at implanting zone and slowly increased with increase of implanting dose. It’s easy to conclude that more vacancies are formed during implantation with increase of dopant dose corresponding to the increase of S parameters. Sharp decrease of S parameters after implantation implies a conversion of annihilation mechanism, which can also be concluded by the S-W plot of all samples as shown in figure 2. S-W plots are useful in detecting the change in the nature of positron trapping defects, since the slope of the plots is a fingerprint of a specific vacancy [22]. For un-doped sample 0#, the S-W parameter changed linearly from surface to the bulk which means a single annihilation mechanism, but for samples 1# to 4#,
double kinds of annihilation mechanism can be found and one of them at (0.0077,0.4457) is believed to be induced by implantation.

The dominant vacancy-type defects in CoTiO films include V_{Ti}, V_{O}, complex involving V_{Ti} or V_{O}, and other impurity. CDB measurements were expected to provide additional information about the atoms surrounding the annihilation site and the results are shown in figure 3. Sample 0#, 1#, 3# and annealed Ti bulk were measured with incident positron energy fixed at 2 keV with the mean depth of 28.5 nm experience calculated by \( d_{\text{ann}} = 40E^{1.6}_{(keV)} / \rho_{(g/cm^3)} \), which is smaller than SRIM results\(^{[21]}\). The surface effect should be surely considered, but there would be much defects generated with increase of dopant dose which traps positrons more effectively. In order to clarify the type of vacancies induced by dopant, ratio curves were made via dividing each measured CDB spectrum by that of sample 0#. Three different zones can be obviously distinguished along the momentum. At zone about \((0~3) \times 10^{-3} m_0c\), positrons annihilated with valence electrons. Zone \((3~10) \times 10^{-3} m_0c\) was believed to be induced by the Ti vacancies where positrons annihilated with 2p electrons of oxygen\(^{[16]}\), because the ratio decreased due to the absence of oxygen for Ti sample. But for samples 1# and 3#, the ratio corresponding to this zone increased since much more Ti vacancies were induced by ion implantation, and also a partial of positrons will be annihilated on constituent oxygen atoms. The prompt peak at \((10~18) \times 10^{-3} m_0c\) should be induced by 3d electrons of Ti and Co\(^{[20]}\). With similar electron structure except for the 3d electrons (Ti: 1s2 2s2 2p6 3s2 3p6 3d2 4s2; Co: 1s2 2s2 2p6 3s2 3p6 3d7 4s2), Co has five more atomic nucleus so that its 3d electron momentum is larger than that of Ti, this leads to the broadening of the prompt peak centered at ~ \(15 \times 10^{-3} m_0c\) compared with that of Ti sample in figure 3. It is interesting that the Ti and substitutional Co at the Ti sites enhanced positron annihilation although they are positively charged, thereby non-trapping centers for positrons. Considering the fact that there are excess Ti 3d electrons around the oxygen vacancy upon ion implantation, the above vacancy complex should be weakly negatively charged. So, these results imply the presence of Ti-Co-V_{O} or Ti-V_{O} complex.

![Fig.3. Ratio curves of CDB results for samples Ti, 1# and 3# to that of sample 0#](image)

4. Conclusion
In summary, we have studied the Co ion implanted rutile TiO\(_2\) samples by positron annihilation Doppler broadening spectroscopy and CDB measurements with variable energy slow positron beam. The S parameters show that the concentration of vacancies is increased with increase of dopant dose and a new type of annihilation mechanism was distinguished by S-W plot. With CDB measurements, we identified the existence of Ti-V_{O} and/or Ti-Co-V_{O} vacancy complex because of the existence of excess Ti 3d electrons around the oxygen vacancy.
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