

FEATURES OF FORMATION OF Cr³⁺ PARAMAGNETIC CENTERS IN STRONTIUM TITANATE (SrTiO₃) IMPLANTED WITH CHROMIUM IONS

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Abstract: We present results of structural (XPS) and magnetic resonance (EPR) studies of single-crystal plates of strontium titanate (SrTiO₃) heavily doped with chromium utilizing ion implantation technique. It was shown that the temperature of the oxide matrix during ion implantation (300 K or 900 K) significantly affects the valence state of the implanted chromium impurity (Cr⁰ or Cr³⁺) and the depth profiles of its distribution in the SrTiO₃ matrix. Using the EPR method, it was established that as a result of implantation of chromium impurity at an elevated substrate temperature during irradiation, the dominating color centers in the surface implanted oxide layer appear in the form of trivalent chromium ions in a cubic environment with a g factor $g=1.976$ and the value of the hyperfine coupling constant with the magnetic nucleus of ⁵³Cr isotope, $A=16.2\times 10^{-4}$ cm⁻¹. From a comparison of these data with parameters for the cubic Cr³⁺ impurity center in the SrTiO₃ single crystal, it was concluded that this center is localized in the structural positions of titanium. Upon implantation of a chromium impurity in SrTiO₃ at room temperature of the substrate, in addition to cubic Cr³⁺ centers, new signals were detected in the EPR spectra, apparently associated with the formation of oxygen vacancies in the implanted oxide. However, the number of these additional centers does not change significantly even after high-temperature heat treatment of samples in air at temperatures up to 900 K. It is noted that signals of this type also appear in the spectra of SrTiO₃ samples obtained as a result of hot implantation and then subjected to high-temperature thermal annealing.

Keywords: strontium titanate, chromium ion, ion implantation, electron paramagnetic resonance, oxygen vacancies, XPS, thermal annealing

Introduction

A lot of research has been devoted to studying the structure, dielectric, magnetic, and spectral properties of oxide single crystals doped with 3d-elements. A wide range of changes in the properties of oxide compounds strongly depends on the conditions of their synthesis and the concentration of impurity ions, as well as on the effect of thermal annealing or high-energy irradiation on them by electrons, protons or ions. Note that a change in the fundamental properties of oxide crystals is often directly related to the formation and presence of oxygen vacancies in their structure [1-4]. Functional impurity centers of chromium in strontium titanate, SrTiO₃:Cr, and the processes of their conversion have been studied for a long time, including the EPR method [5-13]. The EPR spectra of Cr³⁺ ions in chromium-doped SrTiO₃ crystals were observed for the first time in [5], where parameters of the spin Hamiltonian were determined. The behavior of chromium impurities in connection with charge transfer processes in strontium titanate was studied in [6]. Chromium centers associated with an oxygen vacancy are described in [7,8]. The EPR method was also used to control the valence state and structural position of the chromium impurity in SrTiO₃ samples nonstoichiometric in oxygen content [10]. The ESR of tetrahedrally coordinated centers of pentavalent chromium ions Cr⁵⁺ in SrTiO₃ was observed in [13].

This paper presents the results of a study of the formation of EPR-active paramagnetic centers in the surface layer of single-crystal strontium titanate doped with a high concentration of chromium by ion implantation. The effect of the temperature of the irradiated substrate, SrTiO₃, and subsequent post-implantation heat treatment on the depth distribution profiles of the chromium impurity and its valence state, as well as on the type of paramagnetic center formed, is shown.

Samples preparation

Single-charged chromium ions (Cr⁺) with an energy of 40 keV were implanted into single-crystal (100)-oriented SrTiO₃ plates, 10×10×1.0 mm³ in size, to a high dose (fluence) of 5.0×10¹⁶ ion/cm² at a constant ion current density 8.0 μA/cm². The implantation was carried out on an ILU-3 ion-beam accelerator in a residual vacuum of 10⁻⁵ Torr at room temperature (300 K, sample **Cr-ST-1**) or at elevated (900 K, sample **Cr-ST-2h**) temperature of the irradiated oxide substrate. After implantation, the samples were cut by a diamond saw for subsequent structural and magnetic resonance studies, and some of the obtained samples were then subjected to thermal annealing in air at $T_{\text{ann}} = 900$ K for 30 minutes (**Cr-ST-1a** and **Cr-ST-2ha**, respectively).

XPS -analysis

The depth profiling of the elemental composition of samples Cr-ST-1 and Cr-ST-2h implanted with chromium ions was performed. To do this, we used the method of X-ray photoelectron spectroscopy (XPS) utilizing the layer-by-layer etching with argon ions (ion energy of 2 keV, working field of $10 \times 10 \text{ mm}^2$, beam current – $10 \text{ }\mu\text{A}$). The evolution of the shape and intensity of the XPS spectra upon deepening from the sample surface is clearly observed (do not present), and a depth distribution of the concentrations of the implanted impurity and structure-forming elements in the implanted strontium titanate are shown in Figure 1. This data were obtained by an analysis of the intensities of the XPS spectra for various chemical elements (Cr, Ti, or Sr) at various depths, as well as the decomposition of the XPS spectra for the chromium impurity into components corresponding to the contributions of chromium ions of different valences.

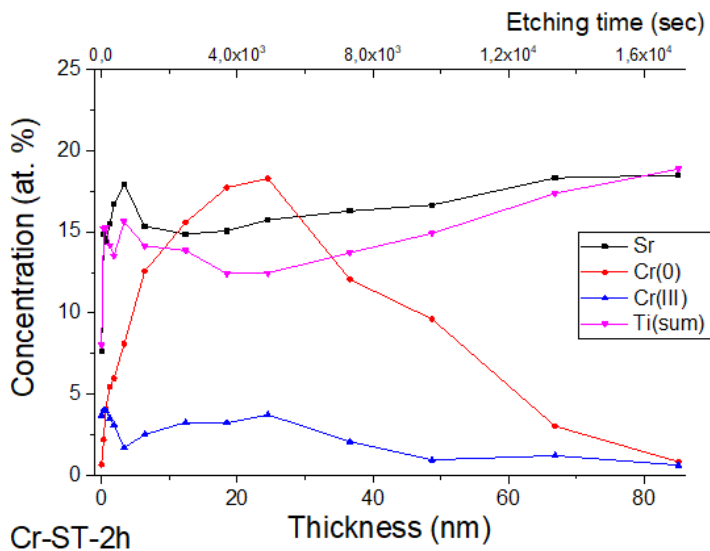
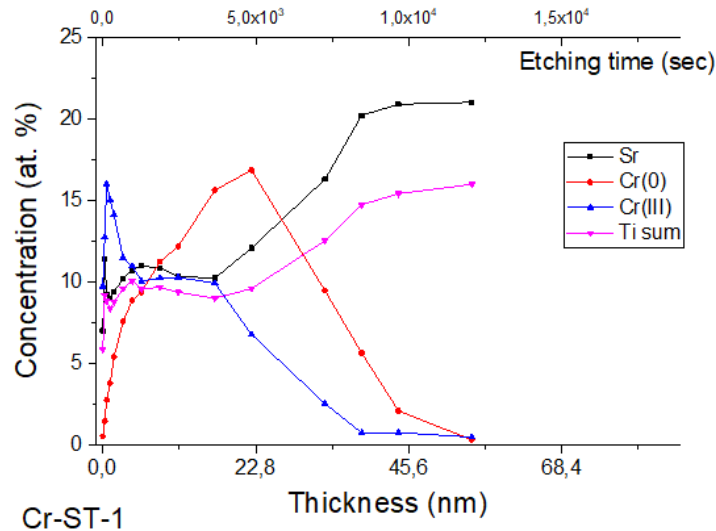


Figure 1. The depth distribution profiles of chromium impurities in different valence states (Cr (0), Cr (III)), as well as for structural elements, Sr and Ti, in the samples: Cr-ST-1 (top figure) and Cr-ST-2h (bottom figure)

It can be seen from the above that the distribution of the chromium impurity is uneven, and there is a peak in the distribution function at a depth of ~ 22.5 nm, which corresponds to the mean free path of 40 keV chromium ions in the SrTiO₃ matrix. In addition, the penetration depth of the chromium impurity into the Cr-ST-2h sample obtained at an elevated irradiation temperature is almost double of that in the Cr-ST-1 sample implanted at room temperature. Although the main part of the impurity was found in the metallic state (Cr⁰), a significant part of the Cr³⁺ is concentrated near the surface of the sample (for Cr-ST-1) or in the extended “tail” of the depth distribution function in the Cr-ST-2h sample. It is important to note that trivalent chromium concentration profiles specularly mirror the Ti concentration profiles in the Cr-ST-2h sample. This result indicates that trivalent chromium replaces Ti⁴⁺ cations in the crystal lattice of strontium titanate.

EPR spectroscopy

Electron paramagnetic resonance (EPR) studies were carried out at room temperature on an EPR spectrometer *EMX/Plus* (Bruker) at X-band (~ 9.4 GHz). The angular dependence of the EPR spectra was measured using an automated programmable goniometer. Both the initial SrTiO₃ substrate and the implanted ones (Cr-ST-1 and Cr-ST-2h), and then sequentially annealed samples (Cr-ST-1a and Cr-ST-2ha), were studied.

An ESR study of the initial SrTiO₃ substrate revealed a small amount of impurity ions Fe³⁺ and Mn²⁺ contained in it. The study of a CrST-2h sample implanted with chromium ions at an elevated substrate temperature showed that the EPR signals corresponding to the implanted Cr³⁺ ions in a cubic environment are observed and dominate (in comparison with the initial substrate containing an Fe³⁺ and Mn²⁺ impurity (Fig. 2). Chromium has four isotopes, but only ⁵³Cr of them has a nonzero nuclear spin $I = 3/2$ (the natural abundance of the ⁵³Cr isotope is 9.5% of the total). Thus, when analyzing the EPR spectra, it is necessary to take into account the influence of the crystal field in which the chromium ion is located, the hyperfine interaction of an unpaired electron, and the interaction with a magnetic field.

The observed spectra are well described by the following spin-Hamiltonian [14]:

$$H = g\beta\mathbf{SB} + \mathbf{SAI}, \quad (1)$$

where the first term describes the Zeeman interaction with a magnetic field, and the second one describes hyperfine interaction with a ⁵³Cr magnetic nuclear. From the analysis of the EPR

spectra (Fig. 2), the values of the spin-Hamiltonian (1) parameters were determined: $g = 1.978 \pm 0.002$, $A = (16.2 \pm 0.1) \times 10^{-4} \text{ cm}^{-1}$.

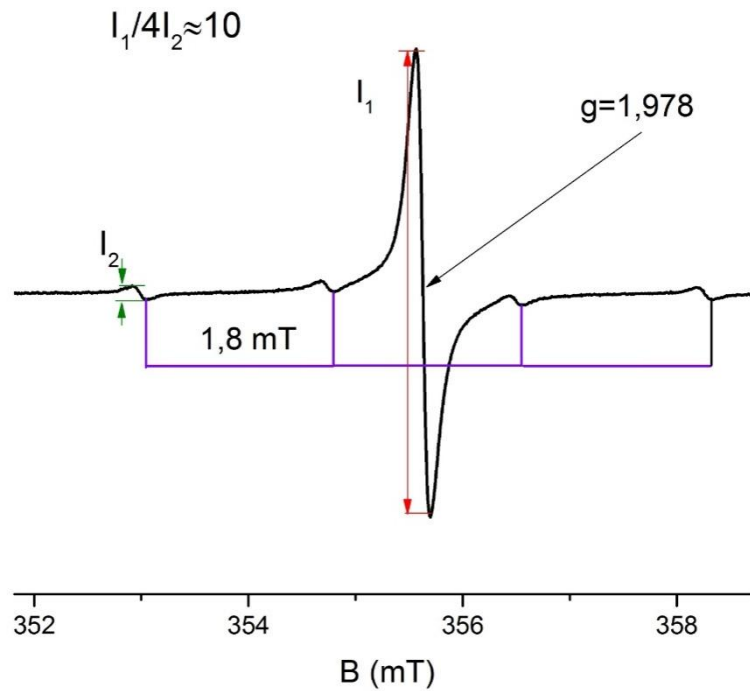


Figure 2. The EPR spectrum of the sample CrST-2h. The ratio of line intensities in the EPR spectrum with hyperfine splitting (I_2) and without hyperfine splitting (I_1) is consistent with the natural abundance of chromium isotopes.

The parameters of this center coincide with the parameters of the cubic center of chromium observed in SrTiO_3 single crystals doped with chromium [5,8]. For the cubic centers of chromium ions in SrTiO_3 single crystals, a dependence of the intensity of the spectra on the illumination of the crystal was observed. This was explained by the fact that in perfect (with good insulating properties) stoichiometric crystals, chromium ions are embedded in the lattice in the Cr^{4+} charge state, replacing Ti^{4+} ions in octahedral positions [8]. Under the influence of daylight, chromium from the valence state of 4+ goes into the 3+ state. This state is unstable, and in the dark it relaxes back to the valence state of chromium 4+ for some time [8].

For implanted single crystals, the intensity does not decrease even after prolonged exposure to darkness. It probably indicates the presence of defects in the crystal, which can compensate for the lack of a positive charge in the strontium site, so that chromium ions can remain in the 3+ charge state immediately after implantation.

New signals appear in the EPR spectrum of CrST-2ha sample after annealing, which are probably related to oxygen vacancies, but the observed signals and their angular dependence (see

Fig. 3) indicate that the nature of the observed additional signals differs from $(\text{Cr}^{3+}\text{-VO})$ centers formed by vacancies in single crystals doped with chromium [5, 8].

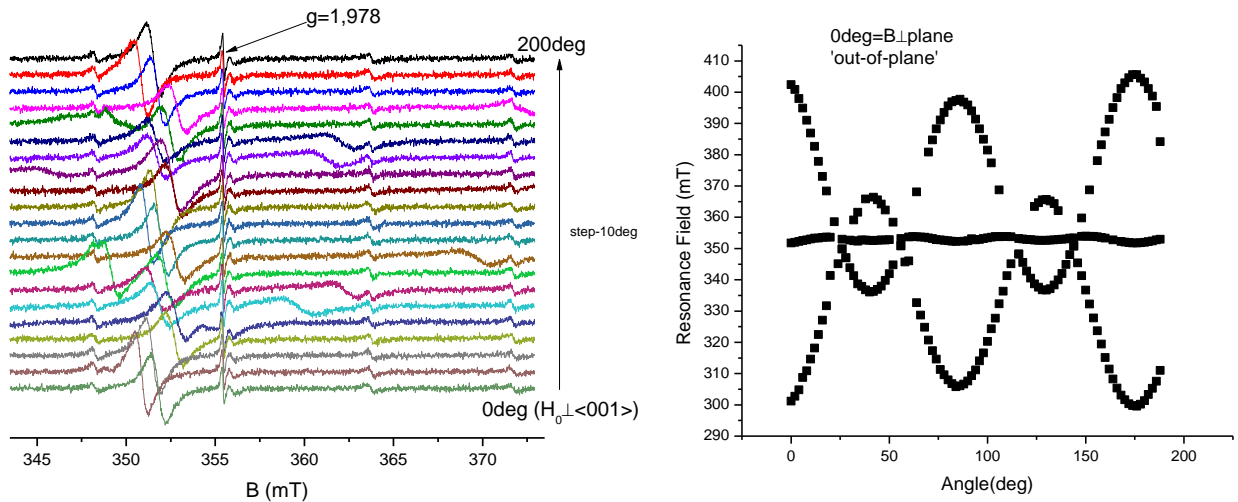


Figure 3. Angular dependence of the EPR spectrum of the implanted and then annealed CrST-2ha sample at room temperature (left window is the evolution of the spectra, right window is the angular dependence of the resonance field of the observed lines). The magnetic field was rotated in the (100) plane of the SrTiO_3 single crystal plate. Microwave frequency is equal to 9.8375 GHz.

It is interesting to note that the same signals were also observed in the CrST-1 sample implanted at room temperature, both before and after annealing. Moreover, their intensity did not significantly change after annealing. More studies are needed to determine the nature of these centers.

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