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# High Resolution Characterization on Point Defects in (Pr,Al) Implanted $SrTiO_3$

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$SrTiO_3$ doped with Pr (STO:Pr) is of special interest because it shows red cathodoluminescence with an efficiency as high as 0.4lm/W at an anode voltage of 400V and an acceptable efficiency at low voltages even below 10V. [1] In addition, by co-doping with a small amount of selected elements such as Al, $SrTiO_3$:Pr becomes a bright phosphor used for field-emission displays and vacuum fluorescent displays. [2] A few possible explanations have been proposed for this increased efficiency. It has been proposed [1] that $Al^{3+}$ ions preferentially locate around $Pr^{3+}$ ions, in order to compensate the charge difference between the $Pr^{3+}$ ions and the host ions, which, as a consequence, improves the crystallinity and changes the crystal field around $Pr^{3+}$ ions. On the other hand, Kutty and Nag [3] attributed such effect to the formation of secondary nano-particles and the associated interfacial defects. However, due to the lack of direct experimental evidence, no clear understanding of rare earth luminescence in this system is available. Here we present first observations of STO:Pr co-doped with Al in order to elucidate the nanoscale structure of these materials.

$Pr^+$ ions were implanted in (001) $SrTiO_3$ single crystals at an energy of 35keV and a dose of $7x10^{13}cm^{-2}$ at room temperature (RT). $Al^+$ ions were implanted subsequently at 15keV to a dose of $3.8x10^{14}cm^{-2}$ at RT. To remove the damage caused by the implantation processes, annealing treatments at 400˚C, 700˚C and 800˚C for 5-180mins were carried out after implantation. Photoluminescence of as-implanted and annealed crystals were investigated using a He-Cd pump laser of 325nm wavelength at RT. Detailed structural characterization was carried out with high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) with an aberration-corrected FEI Titan 80-300 Cubed microscope.

The emission peaks in the photoluminescence (PL) spectra, related to the intra-4f transitions of $Pr^{3+}$ ions, include one broad peak of ~610nm wavelength and several narrow atomic-like peaks. The intensity of the broad peak is greatly enhanced with increasing annealing temperature. In the as-implanted crystals, we observe a 25~30nm thick amorphous layer and 7-15nm thick crystalline layer with a high density of defects (Fig. 1a). Following annealing, the layer with a high-density of defects re-crystallizes at 400˚C with this effect being more pronounced at higher annealing temperatures. In the crystal annealed at 800˚C, the amorphous layer is fully re-crystallized. Cube-shaped nano-clusters of about 0.8-2.4nm size were observed in the implanted regions (Fig. 1b) appearing with a reduced intensity with respect to the STO background. We detected no clusters with higher intensity than the background in HAADF images suggesting that the Pr ions are uniformly distributed rather than in clusters.

In order to understand the site-preference of the $Pr^{3+}$ ions and assess whether a solid solution of STO with Pr ions is present, we carried out visibility tests using multi-slice simulations [4] to identify the imaging and sample requirements for the detection of single atoms in the sample. Our simulations suggest that directly imaging Pr (Z=59) in crystalline $SrTiO_3$ could only be achieved in samples with a thickness less than 5nm (Fig.2) The visibility of Pr in the Al clusters within STO is currently being investigated to assess the relationship between the Pr and Al distributions in the crystals.[5]

References

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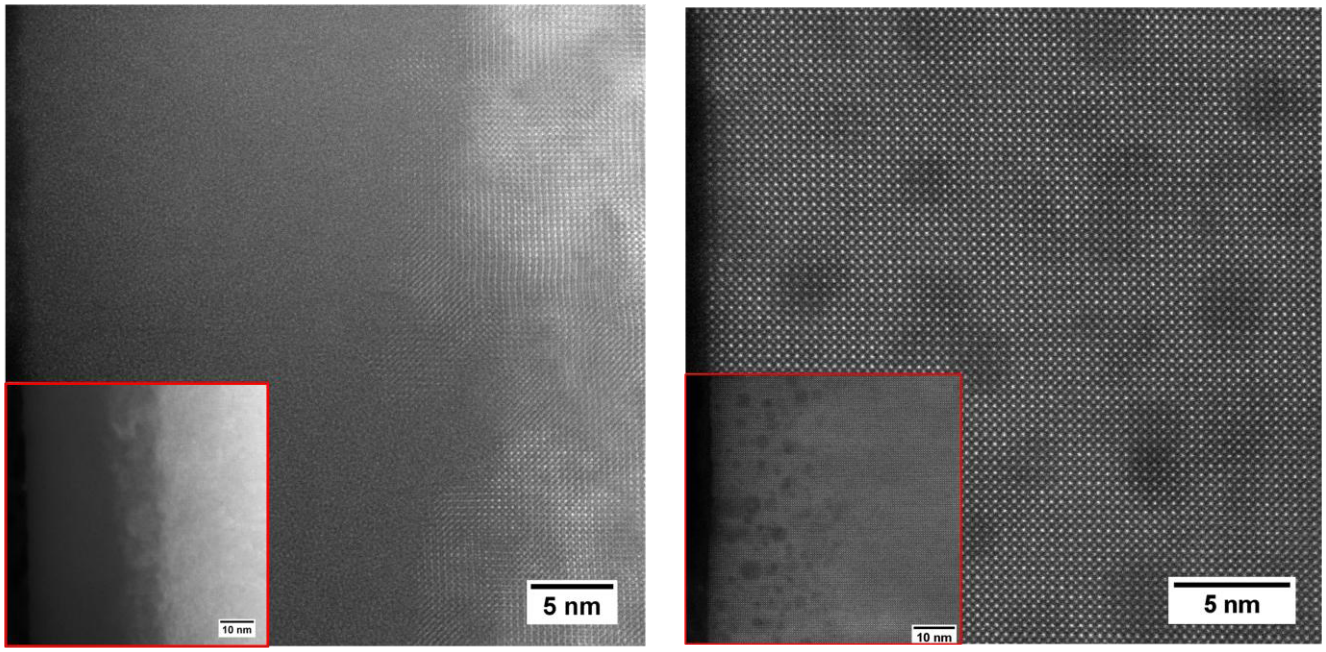


(a) (b)

FIG. 1. STEM-HAADF images of as-implanted (a) and annealed (b) $SrTiO_3$ single crystals annealed at 800˚C for 3hrs. Cross-section wedge specimens were prepared by the low-angle polishing followed by the ion milling with 0.25-1.5keV $Ar^+$ ions. In the inserts, low magnification images showing the field of view and location of the damaged layer.

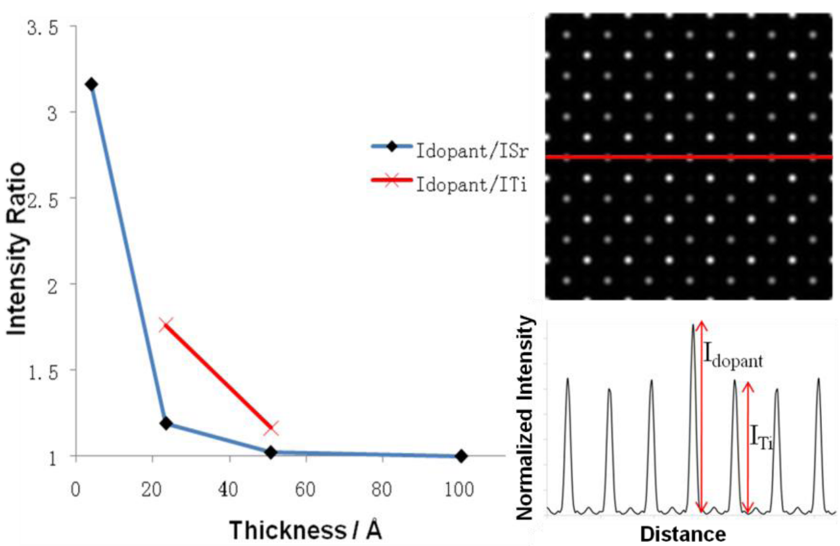


FIG. 2. The visibility of Pr dopants in $SrTiO_3$. The visibility is defined as the intensity ratio between the atomic column that includes the dopant with its neighboring atomic column. In the inset, the HAADF image calculated with a single Pr impurity at the centre of the supercell with the related line scan showing the intensity. The Pr atom is on a substitutional Ti site (red curve) and Sr site (blue curve).

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