Magneto-Optical Characterization on the Ferromagnetic–Paramagnetic Transitions in the Composition-Spread Epitaxial Film of $Sr_{1-x}Ca_xRuO_3$

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To innovate new functional materials, the combinatorial approach with use of composition-spread films[1,2] is promising, since it enables the coherent and systematic investigation of the properties of materials with continuously varying their composition. Perovskite ruthenates investigated here by this approach have recently attracted much attention as high-quality metal-electrode materials for oxide-electronic devices[3,4] and also as correlated metals close to the magnetic instability. The solid solution system of $Sr_{1-x}Ca_xRuO_3$ undergoes a change of magnetism from ferromagnetic ($SrRuO_3$) to paramagnetic ($CaRuO_3$) with doping of x despite of their similar lattice and electronic structures. Many experimental[5–16] and theoretical[17–19] studies have been reported about their critical electronic and magnetic properties. Among them, of particular interest have been the anomalous Hall effect[12–14] and quantum critical phenomena,[15,16] in which critical behaviors of magnetic order play a crucial role. So far, thin films and single crystals with limited sizes and compositions have been synthesized for investigation of $Sr_{1-x}Ca_xRuO_3$. To investigate the magnetic criticality of $Sr_{1-x}Ca_xRuO_3$, the combinatorial synthesis of the composition (x)-spread thin film[20] is most promising. Here, we employed the magneto-optical Kerr spectroscopy to examine the systematics of magnetic properties.

A composition-spread $Sr_{1-x}Ca_xRuO_3$ film was fabricated epitaxially on a $SrTiO_3$ (001) substrate by the pulsed laser deposition method with two ceramics targets of $SrRuO_3$ and $CaRuO_3$. $SrRuO_3$ and $CaRuO_3$ were alternately deposited through a mask moving parallel to the [100] direction of the substrate. The number of laser pulses and the mask position were controlled so as to obtain one unit-cell composition-spread film by one cycle of the depositions, as described in detail in ref. 21. Total thickness of the film was set to be 200 nm (500 unit cells). The substrate temperature was 680 °C and the oxygen pressure during the growth was 70 mTorr. The sample was characterized with four-circle X-ray diffraction. As shown in the lower panel of Fig. 1, the film shows a monotonous change in the out-of-plane lattice constant from 0.388 to 0.394 nm along the [100] direction. By comparing with lattice parameters of bulk and coherently grown films of $Sr_{1-x}Ca_xRuO_3$[13,22] we estimated the composition distribution as $0.13 \leq x \leq 0.53$ (the upper panel of Fig. 1), which agreed well with the independent results of the energy dispersive X-ray analysis.

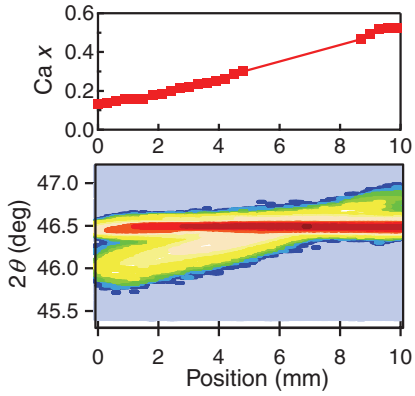

Fig. 1. Characterization of lattice constant in the composition-spread epitaxial thin film $Sr_{1-x}Ca_xRuO_3$ by 2θ scan in four-circle X-ray diffraction. Composition spread, x vs the position, is shown in the upper panel.

We measured the optical reflectivity spectra of the composition-spread thin film of $Sr_{1-x}Ca_xRuO_3$ in a wide photon energy range from 0.1 to 42 eV to deduce the optical conductivity (σ_{xx}) spectra by Kramers–Kronig analysis. For the spectra above 5 eV, the synchrotron radiation at UVSOR facility, Institute for Molecular Science, Okazaki, was utilized as the light source. The room-temperature reflectivity spectra above 5 eV were combined with the low-temperature (e.g., 10 K) spectra below 5 eV to perform the Kramers–Kronig analysis. Magneto-optical (MO) Kerr spec-

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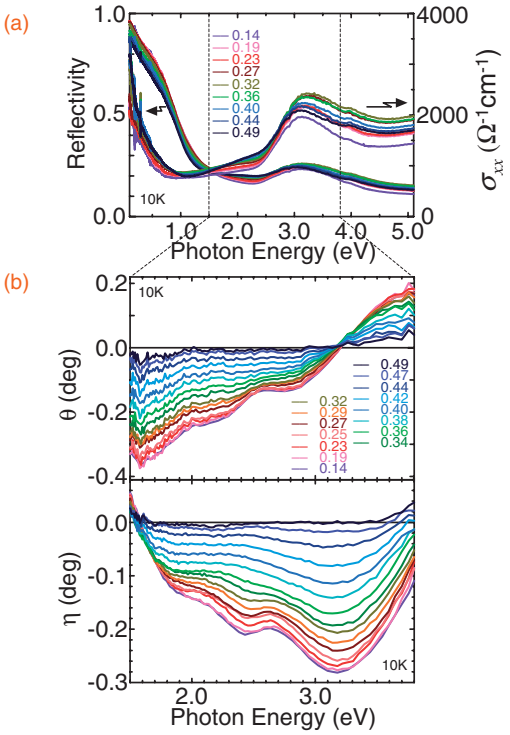

Fig. 2. (a) Reflectivity and optical conductivity spectra, and (b) magneto-optical Kerr rotation (θ) and ellipticity (η) spectra for the composition-spread film of $Sr_{1-x}Ca_xRuO_3$ (x = 0.13 – 0.53) at 10 K.

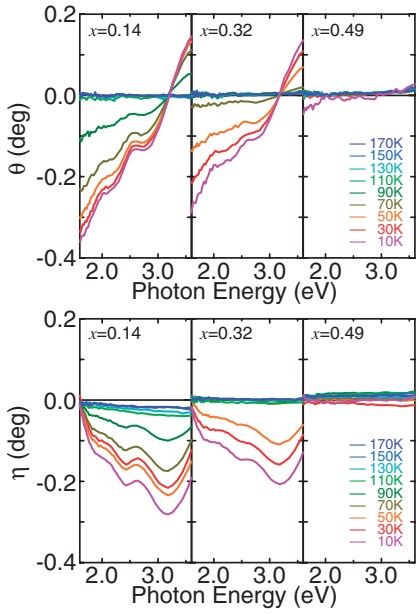

Fig. 3. The temperature dependence of magneto-optical spectra of $Sr_{1-x}Ca_xRuO_3$ with three typical Ca concentrations of x = 0.14, 0.32, and 0.49.

troscopy was performed at 1.5 – 4.0 eV at various temperatures employing the polarization modulation technique.[23] In the MO measurement, monochromatic incident light from a Xe discharge lamp was polarized at 45° through a polarizer and modulated by a photoelastic modulator operated at a frequency of 57 kHz. The light was focused on the sample surface with a spot size of about 700 µm under a magnetic field of 0.2 T applied normal to the substrate (Faraday configuration). The reflected light was detected by a photomultiplier tube through a second polarizer set at 0°. The Kerr rotation and ellipticity were deduced by the f and $2f$ components of signal taken out through a lock-in amplifier and divided by the dc component of signal. The composition (x) dependence of these spectra was obtained by horizontally scanning the light beam spot on the composition-spread film.

Figure 2(a) shows the reflectivity and optical conductivity spectra in the photon energy range of 0.1 – 5.1 eV for $Sr_{1-x}Ca_xRuO_3$ with various x at 10 K. All of the optical spectra exhibit similar metallic features only with minor changes of shapes with x. A broad peak structure observed around 3 eV is assigned to the charge transition excitation between O 2p and Ru 4d t_{2g} states. In Fig. 2(b) the MO spectra of Kerr rotation (θ) and ellipticity (η) are shown for $Sr_{1-x}Ca_xRuO_3$ with varying x at 10 K in the energy region of the charge transfer transition. The spectra exhibit dispersive structures for the charge transfer band around 3.2 eV; the η shows a maximum, while the θ changes sign at the same energy. In the θ spectra, the negative maxima at 1.6 eV is due to the effect of plasmon enhancement, where the real part of diagonal dielectric constant (ε_{xx}) takes the minimum value. In the both θ and η spectra, the spectral magnitude decreases gradually with x while keeping the spectral shape nearly unchanged. This ensures the magneto-optical signals around the charge-transfer excitation to be good probes for the x-dependent magnetic properties.

Figure 3 shows the temperature-variation of the MO spectra of $Sr_{1-x}Ca_xRuO_3$ with three typical concentrations of $x = 0.14$, 0.32, and 0.49. The spectral change observed with increasing temperature exhibits a similar feature to that with increasing x, while the Ca substitution for $SrRuO_3$ suppresses phase transition temperature. The result indicates that the magnitude of MO spectra can be a sensitive probe for the continuous magnetization change also in the thermal process.

The contour maps in the plane of temperature vs composition x as constructed by the magnitudes of θ at 1.71 eV and η at 3.10 eV are shown in Fig. 4. The magnitudes of the MO signals (θ and η) can be viewed as representing the magnitude of the spontaneous magnetization in the present system. The results indicate that the ferromagnetism in $Sr_{1-x}Ca_xRuO_3$ becomes weaker gradually with increasing temperature or x. The continuous change of the ferromagnetic transition temperature can be clearly discerned as it gradually decreases from a maximum curie temperature $T_c \approx 110$ K at the lowest concentration of $x = 0.13$. We note that a finite but small signal is present in η in the low x regime as can be seen in the spectra for $x = 0.14$ in Fig. 3 as well as in the mapping data in lower panel of Fig. 4. However, the boundary due to emergence of ferromagnetism is clearly indicated by the rapid evolution of magnitudes both in θ and η where T_c coincides with the white region in Fig. 4. The phase change from ferromagnetism to papamagnetism at the ground state (e.g., at 10 K) appears also continuous with the increase of x, and hence can be ascribed to the gradual disappearance of the exchange-splitting of the spin-polarized conduction band. The quantum critical point, namely the phase transition point at 0 K, is located around $x = 0.5$ by extrapolation of the track curve.

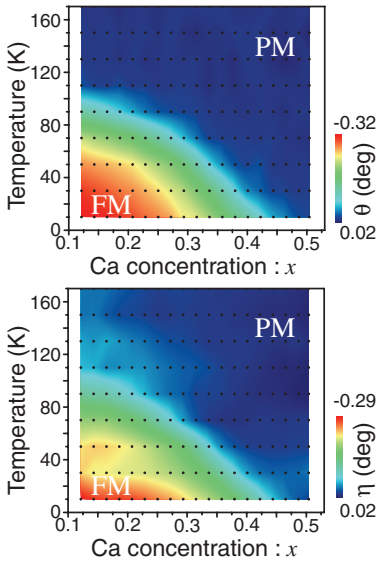

Fig. 4. Contour maps of the ferromagnetic moment in the x–T plane as constructed by the magnitude of Kerr rotation (θ) at 1.71 eV and ellipticity (η) at 3.1 eV for the charge transfer excitation band.

The suppression of the ferromagnetism as observed by the present MO spectroscopy is consistent with the Curie temperatures reported[7–9,11,13–16] for $Sr_{1-x}Ca_xRuO_3$ with x. The difference by about 20 K in Curie temperatures for $x = 0.1$ between our result ($T_c \approx 110$ K) and that reported on thin film samples ($T_c \approx 130$ K)[13–15] as well as the Ca composition of the quantum critical point, around $x = 0.5$ in the present result and $x = 0.7–0.9$ reported by the previous studies,[14–16] may be ascribed to the coherent strain effect induced in the epitaxial growth process of the thin film; the similar reduction of T_c due to the strain effect is already known for $SrRuO_3$.[8,24–26]

In conclusion, we have investigated the systematic variation of the magnetic properties for the composition-spread epitaxial thin film of $Sr_{1-x}Ca_xRuO_3$ by means of magneto-optical Kerr spectroscopy. The x and temperature dependence of the Kerr rotation and ellipticity spectra have revealed the systematic and continuous change of the magnetization due to the variation of the band exchange-splitting. In particular, the continuous transition from the ferromagnetic to the paramagnetic state at low temperatures suggests the quantum critical point around $x = 0.5$ in this epitaxial thin film sample. Our results confirm that the magneto-optical technique is a useful tool to investigate the magnetic state of the combinatorially prepared materials efficiently and systematically.

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