Effects of applied electrical field on electronic structures in LaNiO₃ conductive metallic oxide film: An optical spectroscopic study

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The reflectance spectra of LaNiO₃ film on silicon have been investigated in the wavelength range of 190–2650 nm (0.47–6.5 eV) under different external direct-current voltage. The Drude–Lorentz dispersion model is used to extract the optical function. The O 2p to Ni 3d electronic transition can be uniquely assigned to the energy of about 1.96 eV and decreases with decreasing applied voltage. The discrepancy from the real part of dielectric function with the applied voltage has a strong spectral dependence. The optical conductivity variation under different external voltage indicates that the electrical field can induce the modification of the carrier transport. © *2010 American Institute of Physics*. [doi:10.1063/1.3518493]

In recent years, perovskite and perovskite-related oxide structures have received much attention due to their functionalities as high-temperature superconductors and ferroelectric materials.[1] As we know, top and bottom electrodes play a critical role in optoelectronic and spin-electronic devices.[2–4] Recent studies have shown that metal-oxide electrodes yield capacitors with better fatigue properties than those exhibited by capacitors that use conventional Pt electrodes.[3,4] Metallic oxide LaNiO₃ (LNO) can satisfy the requirements as an electrode as well as a seed layer between the ferroelectric film and substrate. Moreover, LNO has better metallic properties compared with other metallic oxides such as YBa₂Cu₃O₇, La₀.₅Sr₀.₅CoO₃, and SrRuO₃.[5] Nevertheless, there are few reports on dielectric function and optical conductivity of LNO material.[5–9] Although the current-voltage characteristics of metallic oxide have been studied under the illuminations from different light intensities,[10] the voltage dependence of optical properties in a wide spectral range is less reported so far. The purpose of this letter is to investigate the intrinsic relationship between the external electrical field and optical functions in the photon energy range of 0.47–6.5 eV for LNO material.

Nanocrystalline LNO film with a thickness of about 260 nm was deposited on the single-side polished silicon wafers by the modified sol-gel method.[11] A platinum (Pt) layer was sputtered on the edge of the LNO film and two coplanarity electrodes are attached to the ends of the Pt layers. The electrical field was applied with the configuration of out-of-plane during the reflectance measurements. The crystalline structure was analyzed by x-ray diffraction (XRD) using Cu $K\alpha$ radiation (D/MAX-2250V, Rigaku Co.). Figure 1(a) shows that the LNO film presents a polycrystalline structure with the pure perovskite-type phase. The near-normal incident reflectance spectra (about 8°) was recorded in the wavelength range of 190–2650 nm (PerkinElmer Lambda 950). An external direct-current (dc) voltage (*V*) varied from 0 to 20 V (Keithley 2400 source meter) was applied to the LNO film. A three-phase layered model (air/film/substrate) is successfully

used to reproduce the reflectance spectra of the LNO film.[5,12]

The dielectric function can be expressed using a Drude–Lorentz dispersion relation[2,3,5,7,13] $\widetilde{\varepsilon}(E) = \varepsilon_r + i\varepsilon_i = \varepsilon_\infty - [A_D/(E^2 + iEB_D)] + \sum_{j=1}^{5}[A_j/(E_j^2 - E^2 - iEB_j)]$, where ε_∞ is the high-frequency dielectric constant, A_j, E_j, B_j, and E are the amplitude, center energy, broadening of the *j*th oscillator, and the incident photon energy, respectively. A_D is the square of the plasma frequency and B_D is the electron collision or damping frequency. From the reflectance spectra of the LNO film in Fig. 1(b), one can easily identify three evident dips around 3, 4, and 5 eV, a gradual slope around 2 eV, and a steep slope above 6.5 eV. For example, the experimental and fitted reflectance spectra of the LNO film without the applied voltage are plotted in Fig. 1(b). The fitting parameter values are listed in Table I. The reflectance spectra can be roughly divided into two parts, as shown by the dotted line in Fig. 1(b). The low energy one is the Drude region; the other is the so-called charge transfer region, which is typically an energy difference between filled *p* bands of ligand anions and unoccupied upper Hubbard 3d band.[6]

The Drude and charge transfer regions at voltages of 0, 2, and 20 V are shown in Figs. 1(c) and 1(d), respectively.
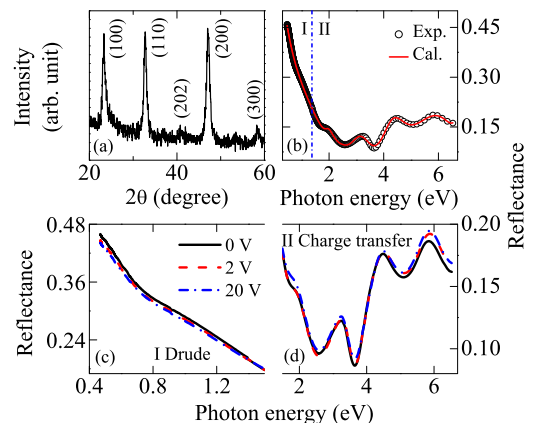

FIG. 1. (Color online) (a) The XRD pattern of the LaNiO₃ film grown on Si substrate. (b) Experimental and best-fit reflectance spectra of the LaNiO₃ film from near-infrared to ultraviolet photon energy region at the voltage of 0 V. (c) Experimental reflectance spectra of the LaNiO₃ film in Drude and (d) charge transfer (d) regions at different applied voltage.

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TABLE I. The parameter values of the Drude–Lorentz model for the LaNiO₃ film are determined from fitting the ultraviolet to near-infrared reflectance spectra under the applied voltage varied from 0 to 20 V.

Voltage (V)	ε_∞	A_D (eV)	B_D (eV)	A_1 (eV)²	B_1 (eV)	E_1 (eV)	A_2 (eV)²	B_2 (eV)	E_2 (eV)	A_3 (eV)²	B_3 (eV)	E_3 (eV)	A_4 (eV)²	B_4 (eV)	E_4 (eV)	A_5 (eV)²	B_5 (eV)	E_5 (eV)
0	0.79	3.96	2.58	0.05	0.38	1.96	0.27	0.94	3.05	0.23	0.91	4.12	0.21	2.03	5.32	0.006	0.57	6.58
5	0.72	3.90	2.42	0.05	0.42	1.94	0.26	0.99	3.03	0.19	0.93	4.10	0.18	2.06	5.32	0.005	0.53	6.56
10	0.70	4.01	2.57	0.05	0.42	1.93	0.24	0.95	3.04	0.20	0.95	4.11	0.16	1.94	5.33	0.003	0.47	6.55
20	0.71	4.06	2.64	0.05	0.43	1.91	0.24	0.97	3.03	0.20	0.96	4.11	0.14	1.86	5.33	0.004	0.55	6.54

Generally, the reflectance with the applied voltage are lower than that with zero voltage in the Drude region, while the situation is reverse in the charge transfer one. In the low photon energy region, we identify a strong Drude response and an incoherent background up to about 1.5 eV. This is the energy range where effective low energy physics in terms of polarons or the orbital liquid dominates.[14–17] In the LNO system, the charge transfer excitations from the bands involving oxygen 2p states to the bands involving nickel 3d states are found above the photon energy of 1.5 eV.[6,18] The local charge transfer energy to move an electron from the O^{2-} ion to the Ni^{3+} ion is essentially given by the difference in the ionization potential of O and the electron affinity of Ni in the actual solid. Therefore, the charge transfer energy can be estimated below 8 eV due to the effects.[15,19,20] The optical transition peaks of the LNO material without the applied voltage are located at 1.96 ± 0.05, 3.05 ± 0.10, 4.12 ± 0.25, 5.32 ± 1.24, and 6.58 ± 5.05 eV, respectively. Note that the fifth transition (E_5) is in good agreement with the peaks at 4.5–6.5 eV estimated from the U+GW approximation[21] and the experimental observation.[6,22,23] The higher-lying excitation around 6 eV is related to O 2p to La 5d excitations.[6] In experimental spectrum of LaNiO₃, there are Ni 3d and La 5d at 0–2 and 6–8 eV, respectively,[22] which is consistent with the peaks at the similar region by the U+GW approximation.[21] Taking into account that the first (1.96 eV) and fifth (6.58 eV) peaks of the present observations are located in the region of 0–2 and 6–8 eV, we can assign them as the electronic transitions of O 2p to Ni 3d and La 5d, respectively. Note that the O 2p to Ni 3d excitation energy position decreases with decreasing applied voltage, while other excitations show no evident variation trend. It indicates that the external electrical field mainly affects the O 2p to Ni 3d excitation in the low energy region.

Figures 2(a) and 2(b) show the real part of dielectric function ε_r and optical conductivity σ_r of the LNO film recorded at various applied voltages between 0 and 20 V. The applied voltage predominantly affects the real part ε_r in the photon energy region from 0.47 to 4 eV, while in the high energy region (4–6.5 eV), there is no evident change. The real parts of dielectric function decrease considerably with the applied voltage from the first (1.96 eV) to the third (4.12 eV) center energy of the Lorentz oscillators. This is likely because the high applied voltage reorients the LNO crystalline structure.[24] Figure 3(a) presents the difference of the real part of the dielectric function $\Delta\varepsilon_r$ between the zero voltage and 2, 10, and 20 V at different photon energies. The $\Delta\varepsilon_r$ increases with the applied voltage from 1.5 to 4 eV, which indicates that the applied voltage could decrease the real part ε_r in the photon energy region. The number of excited carriers increases with the applied voltage, which makes the $\Delta\varepsilon_r$ a striking variation. However, the $\Delta\varepsilon_r$ under the highest voltage of 20 V is smallest and the value at the lowest voltage of 2 V is largest below 1.5 eV. Interestingly, the $\Delta\varepsilon_r$ is negative in the high energy region of 4–6.5 eV. That is to say, the voltage dependence of the ε_r could be divided into three regions: <1.5, 1.5–4, and 4–6.5 eV, which are roughly corresponding to the different excitations.

The applied voltage remarkably affects the optical conductivity in the high energy region of 4–6.5 eV. The difference of the optical conductivity between zero voltage and 20 V around each center energies of four Lorentz oscillators is 39 (1.96 eV), 86 (3.05 eV), 176 (4.12 eV), and
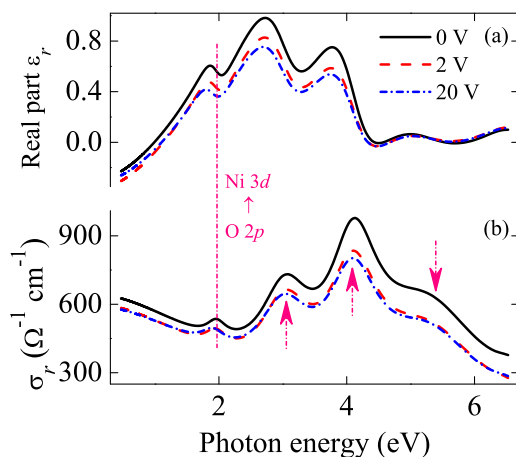

FIG. 2. (Color online) Real parts of (a) dielectric function and (b) optical conductivity for the LaNiO₃ film at different applied voltage. Note that the dashed line indicates the assignment from the electronic transitions and the arrows show other potential transitions.
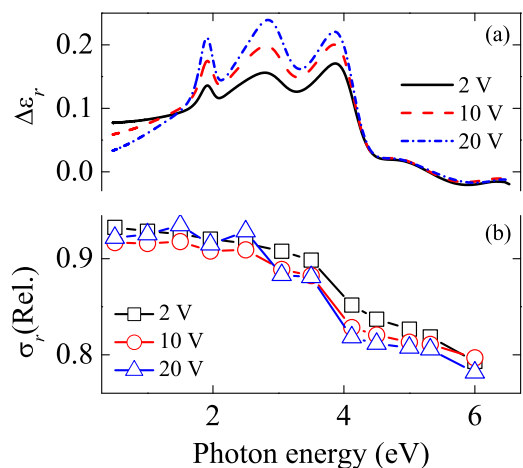

FIG. 3. (Color online) (a) The difference for the real parts of dielectric function between zero voltage and 2, 10, and 20 V at different photon energies. (b) Real part of optical conductivity for the LaNiO₃ film. Note that the data have been normalized by that at zero voltage.
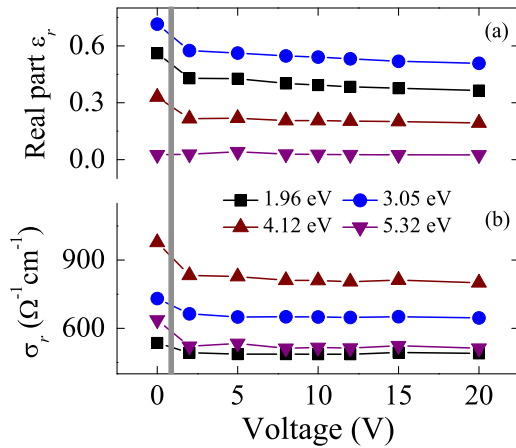
FIG. 4. (Color online) Real parts of (a) dielectric function and (b) optical conductivity are varied as the applied voltage at four center energies of the Lorentz oscillators for the LaNiO₃ film. Note that the optical constants generally decrease when an external voltage is applied.

131 Ω^{-1} cm^{-1} (5.32 eV), respectively. Figure 3(b) shows that the optical conductivity spectra at various external voltages have been normalized by that at zero voltage. The relative σ_r decreases with the applied voltage at 3.05, 4.12, and 5.32 eV. A frequency-dependent real part of the conductivity is maximum at zero frequency, known as dc conductivity σ. As we know, the drift velocity is proportional to the applied voltage V. After obtaining energy from the applied electric field, the free carriers transmit energy to crystal lattice by emitting phonon. The increased applied voltage results in an increase in the electron velocity, suggesting decreased mobility of electrons in the high energy region.

The real part of dielectric function and optical conductivity decreases considerably with the applied voltage and the voltage dependence is summarized in Figs. 4(a) and 4(b). Figure 4(a) shows that the real part of the dielectric function is varied as the applied voltage at four center energies of the Lorentz oscillators. All the ε_r decrease evidently under the applied voltage, except for ε_r at 5.32 eV. The decrease in optical conductivity with increasing external voltages indicates that the applied voltage gives rise to a modification of the free electron behavior. A similar phenomenon has been observed previously in semiconductor GaAsN.[25] Note that the chemical bonding in the LNO is not purely ionic, but shows substantial covalent (Ni–O and La–O) and metallic (Ni–O–Ni) parts.[15] Therefore, the bond strengths of the LNO material can be affected by the external electrical field and further provide the perturbations on the electronic states. It results in the distinguishing optical response behavior under different applied voltages for the LNO film. On the other hand, a passage of an electrical current through the LNO film releases heat under the applied voltage, which is proportional to the square of the voltage divided by the resistance of the LNO film (about 185 Ω). Moreover, the maximum value of Joule heating and temperature increasing can be estimated to about 2.2 W and 20 K with the reported specific heat capacity of the LNO material, respectively.[26] The temperature variation effect on the optical response could be minor for the LNO film during the application of the dc voltage. Therefore, the optical conductivity variation under different exter-

nal voltage indicates that the electrical field and its evoked Joule heat can result in the modification of the free carrier transport behavior.

In conclusion, the optical properties of the LNO film have been investigated. It was found that the real part of dielectric function and optical conductivity show the strong spectral dependence under the external electrical field.

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