Field emission properties of Si tip arrays coated with N-doped SrTiO$_3$ thin films at different substrate temperature

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The effect of substrate temperature ($T_S$) on the behavior of field emission, microstructure, optical band gap, and the surface energy of N-doped SrTiO$_3$ thin films coated on silicon tip arrays has been examined in detail. Results indicate that the $T_S$ dominates the chemical states of nitrogen added to the sputtered SrTiO$_3$ films and hence the observations. At the critical temperature of 600 °C, nitrogen atoms incorporate into the oxide film with $sp$-hybridization features. The generation of the nonbonding lone pair states lowers the optical band gap and the lone pair induced antibonding dipoles lower the threshold field for electron emission substantially. At lowered $T_S$, molecular adsorption of nitrogen dominates. Contact angle measurements further evidence for the presence of antibonding dipole states at the surfaces which is responsible for the adsorbate-induced surface stress.

II. EXPERIMENTAL DETAILS

The N-doped SrTiO$_3$ thin films were deposited on Si tip arrays using Leybold UNIVEX450B multieathode rf magnetron sputtering system. A 3 in. stoichiometric SrTiO$_3$ ceramic plate of 99.9% purity was used as sputtering target. The process chamber was evacuated to the pressure as low as $10^{-6}$ mbar before deposition. The gas used in this work was a mixture of Ar and N$_2$ with Ar-to-N$_2$ ratio of 1:1. rf power and sputtering pressure were maintained at 200 W and 1.6 × 10$^{-2}$ mbar, respectively, in this work. The films were deposited at different substrate temperatures of 400, 500, 550, and 600 °C separately. The deposition time is 90 min with a growth rate of 1.33 Å/min. The thickness of N-doped SrTiO$_3$ thin film is about 12 nm.

The electron FE of coated Si emitter arrays was measured in a parallel plate configuration with anode-to-sample spacing of 50 μm using a Teflon spacer. A piece of indium tin oxide glass with a sheet resistance of 10 Ω/□ was used as anode to collect the emitted electrons. During character-
ization, the vacuum in the measurement chamber was main-
tained at $10^{-6}$ mbar using a turbomolecular pump. The em-
tered current flow as the function of applied voltage was
recorded via a home-designed automatic characterization
system. In the stability measurement, the emission current
flow was maintained at around $1\times10^{-9}$ A and the current varia-
tion was recorded for 1800 s with an interval of 2 s.

The crystal structure of the sputtered N-doped SrTiO$_3$
films was investigated using Siemens XRD scans with a
scanning rate of 2°/min. The surface energy of the each
sample was determined by contact angle measurement. The
measurement was performed at room temperature in the at-
ompheric ambient using a commercial contact angle meter
(Dataphysics OCA 20) with experimental error of 1°. The
optical band gap of the sputtered N-doped SrTiO$_3$ films was
deduced using Woollam variable angle spectroscopic ellip-
someter in the wavelength range of 270–800 nm with 2 nm
interval. The nitrogen chemical bond states are studied by
XPS measurement, which was performed using a VG ES-
CALAB 220i-XL instrument with Al $K\alpha$ x-ray source
(1486.6 eV). The pass energy of the analyzer was set to
20 eV to achieve high measurement accuracy. The binding
energy was referenced to the C 1$s$ line at the binding energy
of 285.0 eV.

### III. RESULTS AND DISCUSSION

Figure 1 shows the XRD profiles of the sputtered N-doped SrTiO$_3$ films as a function of substrate temperature. Experiment showed that the 12-nm-thick SrTiO$_3$ film is too thin to be detected by XRD, so the 36-nm-thick films were deposited to examine the influence of $T_s$ on the structural evolution of the films. The XRD data show that the N-doped SrTiO$_3$ thin films possess perovskite structure with the strongest peak (110) at 31.5°, which is similar to that of the polycrystalline SrTiO$_3$ films. The intensity of diffraction peaks increases with $T_s$. However, when the $T_s$ is increased to 600 °C, the intensity of diffraction peak of 31.5° becomes weaker and some other peaks appear, corresponding to (111) and (220) planes. The structure evolution can be attributed to the competition between the thermal-activated crystal-grain growth and N corporation in perovskite structure at high temperature.

Figure 2 shows the XPS survey spectrum of sputtered N-doped SrTiO$_3$ thin films deposited at 600 °C, which matches well the standard spectrum of bulk SrTiO$_3$ with an addition of the nitrogen peak. No other impurity elements except for carbon C 1$s$ at 285 eV. The N 1$s$ core level photoelectron spectra in Fig. 3 show two nitrogen doping states in the N-doped SrTiO$_3$ films deposited at different substrate temperatures. When the $T_s$ is increased from 400 to 550 °C, only a broad higher-binding energy peak at around 404.6 eV appears. It is ascribed as the poorly screened final state for molecularly chemisorbed N$_2$, which is confined under the oxide layer or literally adsorbed on the film surface. When the $T_s$ increased to 600 °C, the lower-binding energy around 396 eV also appears corresponding to atomic $\beta$-N state bonding with Ti. The presence of lower-binding energy...
N 1s indicates that Ti–N bonds are formed by the substitutional replacement of O atom by N at high $T_S$ of 600 °C. The result of different nitrogen bonding states in the SrTiO$_3$ thin films can also provide experimental evidence for the XRD result at 600 °C. The nitrogen atomic substitution in SrTiO$_3$ lattice might distort the perovskite structure of the films, resulting in suppression of the polycrystalline perovskite grain growth at 600 °C. So there is a competition on perovskite structure grain growth between the promotion induced by high deposition temperature and the suppression induced by nitrogen substitution in SrTiO$_3$ lattice. From the N 1s core level spectrum, it is seen that the nitrogen bonding states in the N-doped SrTiO$_3$ films are sensitive to the deposition temperature, which may affect the Fermi level, microstructure, and the surface energy of N-doped SrTiO$_3$ thin films.

The variation in the band gap of N-doped SrTiO$_3$ films deposited at different substrate temperatures was investigated by ellipsometer spectra. Figure 4 shows the $(ahv)^2$ versus photon energy $(h\nu)$ derived from the ellipsometer spectra of SrTiO$_3$ thin films deposited at different substrate temperatures, where $a$ is the absorption coefficient, $h$ is Planck’s constant, and $\nu$ is the photon frequency. The band gap energy $E_g$ of the SrTiO$_3$ film can be estimated by applying the Tauc relation

$$
(ahv)^2 = C(h\nu - E_g),
$$

where $C$ is a constant. The band-gap energies of the thin films can be obtained by extrapolating the linear portion of the curves relating $(ahv)^2$ and $h\nu$ to $(ahv)^2=0$. The value of optical band gap of N-doped SrTiO$_3$ films deposited at 600, 550, 500, and 400 °C can be determined around the values of 3.86, 4.21, 4.23, and 4.29 eV, respectively. The relation between the optical band gap and $T_S$ is inserted in Fig. 4. It is seen that the optical band gap decreased gradually when nitrogen are molecularly absorbed in the films at substrate temperature from 400 to 550 °C. Upon nitrogen substitution in SrTiO$_3$ lattice at 600 °C, the band gap decreased rapidly from 4.21 to 3.86 eV. The decrease in optical band gap is believed to be mainly attributed to nitrogen incorporation in SrTiO$_3$ lattice at higher $T_S$. When nitrogen atoms substitute oxygen sites to be bonded to Ti, the corresponding N 2$p$ states are located above the valence band edge. Mixing of N 2$p$ state with O 2$p$ state results in a reduction in the band gap of the N-doped SrTiO$_3$ which coincide with the result of optical band gap as we discussed above. However, as for the N-doped SrTiO$_3$ thin films deposited below 550 °C, nitrogen dopants are only molecularly chemisorbed with poorly screened and hardly interact with the band state of SrTiO$_3$ in the lattice, and thus are unlikely to be effective for narrowing the band gap. So the slight decrease in band gap will be attributed to the growth of perovskite structure grains; however, the rapid decrease may be induced by the nitrogen substitution in SrTiO$_3$ lattice.

The FE characteristics of the silicon tip arrays coated with the N-doped SrTiO$_3$ films deposited at different substrate temperatures are shown in Fig. 5. The emission threshold electric field is defined here as the electric field at which the emission current density reaches $10^{-2}$ $\mu$A/cm$^2$, corresponding to the signal-to-noise ratio of 1000:1. From the $J$-$E$...
curves in Fig. 5(a), it can be seen that the FE behavior is highly correlated with the $T_S$. With increasing the $T_S$ from 400 to 600 °C, the threshold electric field for electron emission of the N-doped SrTiO$_3$ films is reduced gradually from 30.57 to 17.37 V/μm. The threshold electric field results listed in Table I showed that high $T_S$ is more favorable to improve the FE properties.

From FN theory, the decrease in threshold electric field may originate from the reduction in effective work function ($\phi = \phi / B \beta$) of the N-doped SrTiO$_3$ films coated on silicon tip arrays with the same field-enhancement factor $\beta$. Here, the emission data are analyzed using the FN equation:

$$I = A V^2 \exp(-B \phi^{3/2}/V),$$

where $A$ and $B$ are constant, $I$ is the emission current, and $\phi$ is the effective work function of the FE emitter. The FN plots, i.e., log($I$/$V^2$) versus $1000/V$, of the silicon tip arrays coated with N-doped SrTiO$_3$ films as a function of substrate temperature are given in Fig. 5(b). It is found that their FE behavior follows the FN characteristic very well. From the linear fitting to the FN plots, the effective work function of N-doped SrTiO$_3$-coated silicon tip arrays can be deduced by:

$$\phi_{STO} = \phi_{Si}(FNSL_{STO}/FNSL_{Si})^{2/3},$$

where $FNSL$ is the slope of FN plot. By using the FN slope data listed in Table I and silicon work function of SrTiO$_3$ thin films, the effective work function of silicon tip arrays with N-doped SrTiO$_3$ coating is reduced when N is bonded to Ti, which is believed to induce the antibonding state to reduce the work function and the lone pair states that narrow the band gap. The decreased effective work function was about 0.73 eV. Therefore, the presence of antibonding states is of virtual importance to the N-enhanced FE and the $T_S$ of 600 °C is critical for the N reaction with the oxide.

The lone-pair dipoles and antibonding dipoles induced by nitrogen doping can result in the strong localization and dipole electrons at surface of thin films. Such charge redistribution and polarization could be responsible for the adsorbate-induced surface stress and the corresponding reconstruction. Here, we also characterize the surface energy of N-doped SrTiO$_3$ thin films using contact angle measuring to study the nitrogen doping effect. Figure 6 demon-

![FIG. 6. (Color online) Variation in the threshold electric field for electron emission (■) and the water contact angle (★) of SrTiO$_3$ thin films deposited at different substrate temperatures.](image)
strates the contact angle of the films deposited at different substrate temperatures and the threshold electric field is also plotted for comparison. It is shown that the contact angle has a maximum value upon nitrogen doping into the SrTiO₃ lattice and has an opposing trend compared to threshold electric field by N addition. Figure 7 illustrates the time-field by N addition.

The stability of emission current is one of the important concerns in practical application of silicon-tip arrays coated with N-doped SrTiO₃ thin films. Figure 7 illustrates the time-dependent emission characteristics for various samples coated N-doped SrTiO₃ thin films deposited at different substrate temperatures. Note that the emission current was investigated at the current level of 1 μA in the beginning. It is clear that the film deposited at 600 °C shows a stable emission for 1800 s. In contrast, the films deposited at lower substrate temperatures and the threshold electric field is also investigated at Tₚ for comparison. We also use the coefficient of variation. The corresponding average electrical current I, standard deviation ΔI, and the coefficient of variation (CV =ΔI/I) are also listed in Table I. From the calculated data, it is found that the film deposited at 600 °C had a minimum CV value of 19.28% which showed a more stable emission current compared than those deposited at lower temperatures. Also when the substrate temperature is decreased to 500 and 400 °C, the coefficient of variation in the emission current dispersion is increased to 53.85% and 59.06%, respectively.

**IV. SUMMARY**

The enhanced FE behavior of silicon tips coated with SrTiO₃ thin films as a function of Tₚ in a mixture ambience of Ar+50%N₂ was studied. The threshold electric field of each sample decreases with the increase in Tₚ and reaches a minimum value of 17.37 V/μm at 600 °C. This enhanced FE characteristics of N-doped SrTiO₃-coated silicon tip arrays are attributed to the reduction in effective work function which decreases to 2.09 eV. The optical band gap of N-doped SrTiO₃ thin film also decreases with Tₚ increasing. The Tₚ enhanced FE behaviors and optical band gap should originate from the different states of doped nitrogen. From XRD and XPS results, the polycrystalline grain grows along with increasing Tₚ. When the Tₚ is increased up to 600 °C, the N-doped SrTiO₃ thin film exhibits well-developed perovskite microstructure and atomic nitrogen is doped into SrTiO₃ lattice. Nitrogen substitution in films will reduce the effective work function of silicon field emitter and then enhance the FE properties according to the bonding and band-forming model. This model may provide a more feasible mechanism for this N-enhanced FE because of the presence of nonbonding lone pair of nitrogen which can induce an antibonding state above the Fermi level to reduce the work function. Water contact angle measurements provide further evidence for the presence of antibonding state induced by nitrogen doping. The emission current stability test shows that at Tₚ of 600 °C, a high and stable emission current can be achieved.