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Electron emission of silicon field emitter arrays coated with N-doped $SrTiO_3$ film

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Abstract Nitrogen doped $SrTiO_3$ (STO) thin films have been fabricated on Si field emitter arrays (FEAs) using reactive RF magnetron sputtering in Ar-N_2 mixture ambient for electron emission applications. The nitrogen incorporation in STO films was revealed both in Fourier transform infrared (FTIR) spectroscopy and in Auger electron spectroscopy (AES). Low dose incorporation of nitrogen in STO films shows enhanced crystallinity, whereas the overdosed films show the degraded perovskite structure. The results demonstrate that the threshold emission field is lowered tremendously from 36.24 V/μm for uncoated FEAs to 17.37 V/μm for 30-nm-thick STO coated FEAs deposited in 50% N_2 ambient. The enhanced electron emission characteristics are highly correlated with the nitrogen incorporation in STO and film thickness. The substitution of nitrogen for oxygen may result in the band-gap narrowing in STO with enhanced electron emission. The thickness dependence might be related to the formation of space-charge-induced band-bending interlayer at STO/Si interface.

Keywords $SrTiO_3$ thin film · Electron emission · Nitrogen doping · Sputtering

1 Introduction

In recent years, Si field emitter arrays (FEAs) have been much more attractive in vacuum microelectronics due to the available state-of-the-art micro-fabrication technology. Surface modification on the Si FEAs is one of the desired technical routes to achieve low operating voltage, high and stable emission current. Kang [1, 2] and Zhu [3, 4] reported that Si FEAs modified by sol-gel $Ba_{0.66}Sr_{0.33}TiO_3$ (BST) ferroelectric thin film could exhibit tremendous enhancement in electron emission current. It is found that the enhanced emission behavior is highly correlated with their microstructure [1, 4], and the film with well-developed perovskite grains is desired to achieve low threshold emission field. The emission behavior is also dominated by their stoichiometric composition [3], which may affect the electronic structure in the films. It is known that electronic defects in the films could be induced via either controlling non-stoichiometric composition or introducing transition metal dopant. The typical transition metal dopant like La^{3+} or Nb^{5+} is usually employed to substitute $Ba^{2+}(Sr^{2+})$ or Ti^{4+} sites in BST films respectively. Recently, substitution of a non-metallic atom such as nitrogen for oxygen in $SrTiO_3$ (STO) [5] and TiO_2 [6] has proven to be indispensable for band-gap narrowing because its p states contribute to the band-gap narrowing by mixing with O $2p$ states. In this paper, we report the fabrication of nitrogen-doped STO thin film on n-type Si FEAs with enhanced electron emission characteristics. The films were deposited using reactive RF magnetron sputtering in Ar-N_2 mixture ambient. Electron emission characteristics of these STO-coated Si FEAs were investigated by changing the coating thickness and nitrogen content in sputtering process, and the corresponding mechanisms were also discussed.

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2 Experimental

STO thin films incorporated with nitrogen were deposited onto n-type Si FEAs using Leybold UNIVEX450B

multi-target RF magnetron sputtering system. The deposition was performed at 600°C from 3-inch stoichiometric STO ceramic target in Ar-N_2 gas mixture with a sputtering pressure of 1.6×10^{-2} mbar. The N content in the films was varied by changing the nitrogen-to-argon flow rate. The fabrication of n-type Si FEAs was detailed in our early publication [3] via conventional photolithographic patterning, silicon anisotropic etching, oxidation for tip sharpening, and buffered oxide etching. The resistivity of Si wafer used is 2–5 Ωcm and the tip height was controlled around 1 μm. Before coating STO layer, the Si FEAs were cleaned in buffered HF solution to remove native oxide layer. The thickness of sputtered STO films was controlled according to the calibrated sputtering rate, which was measured using Filmetrics F20 (Filmetrics, Inc.).

A Siemens X-ray diffractometry (XRD) with a glancing-angle thin film attachment was used to investigate the structural evolution of sputtered STO films in different sputtering ambient. The nitrogen incorporation in STO thin films were characterized using Fourier transform infrared (FTIR) spectroscopy and Auger electron spectroscopy (AES). Field emission characterization was carried out in a diode configuration in a vacuum chamber of 10^{-7} mbar using our home-designed automatic characterization system [4]. The turn-on voltage was defined using an arbitrary criterion with a current density of 10^{-8} A/cm^2, corresponding to the signal-to-noise ratio of 1000.

3 Results and discussion

3.1 Structure of sputtered STO thin films

The X-ray diffraction of sputtered STO films incorporated with nitrogen was investigated as a function of film thickness and nitrogen content in sputtering ambient respectively.

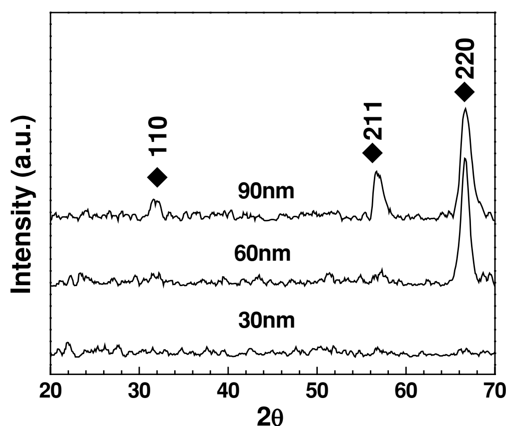


Fig. 1 XRD patterns of sputtered STO films on Si with different thickness, deposited at 600°C in Ar-50%N_2 ambient

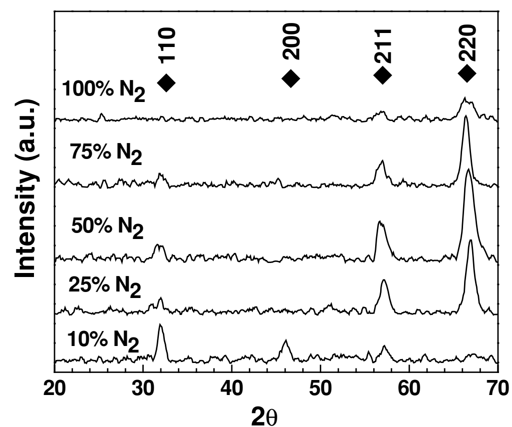


Fig. 2 XRD patterns of 30-nm-thick STO films on Si deposited at 600°C in different nitrogen content ambient

Figure 1 illustrates the thickness dependent structural evolution of these N-doped STO films, which were deposited at 600°C in Ar-50%N_2 ambient. It is shown that there is no peak appearing in the films below 30 nm. It is believed that these films are still at the nucleus formation stage and probably the formatted nuclei are nano-structured with very fine size. With thickness increasing, the peaks of perovskite STO phase clearly appear in their XRD patterns. Therefore, the influence of nitrogen content in sputtering gas on the structural evolution is demonstrated based on the XRD patterns of the 90-nm-thick films, as shown in Fig. 2. The film deposited in 10% N_2 ambient possesses a typical XRD pattern with the strongest (110) peak at 31.5°, which is similar to that of the polycrystalline STO films. However, it is found that the crystallinity of the films is enhanced due to nitrogen incorporation in STO perovskite structure. The film deposited in 50% N_2 ambient exhibits the highest crystallinity. With further increasing nitrogen content to 75% and 100%, the diffraction peaks are broadened and weakened gradually. It is indicated that perovskite structure cannot be maintained due to overdosed nitrogen in the films, and development of STO perovskite structure is impeded accordingly.

However, the XRD is difficult to demonstrate the direct evidence for the nitrogen incorporation in ultra-thin STO films. Therefore, FTIR and AES were performed to specify the chemical bonds and compositional distribution in N-doped STO films. Figure 3 demonstrates FTIR transmittance spectra of 30-nm-thick STO films deposited in different sputtering ambient with nitrogen content from 10% to 100%. The spectrum of STO film sputtered in pure Ar ambient is also shown as reference. There are two major absorption peaks observed in all these STO films sputtered in Ar-N_2 mixture ambient. The peak at 1070 cm^{-1} is attributed to Ti-N bonding [7] and another peak at 480 cm^{-1} is due to the longitudinal optic (LO) phonon mode of STO perovskite [8]. The presence of Ti-N bonding vibration is a convinced evidence to

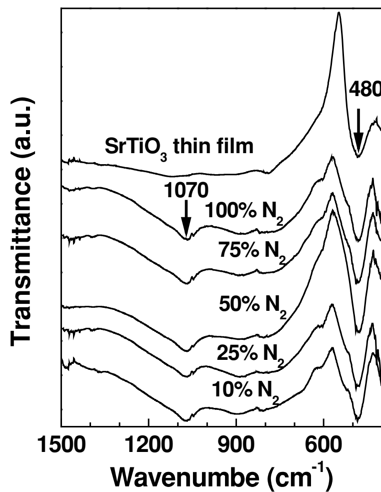


Fig. 3 FTIR spectroscopy of sputtered STO films on Si deposited at 600°C in different nitrogen content ambient

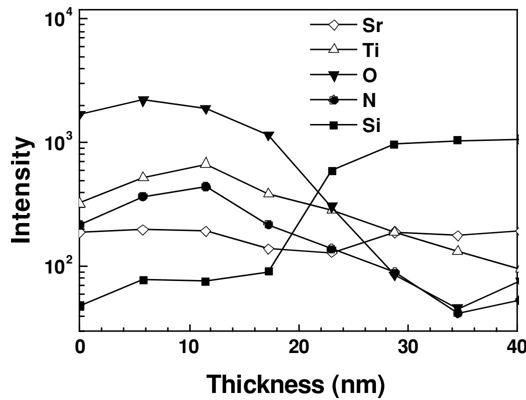
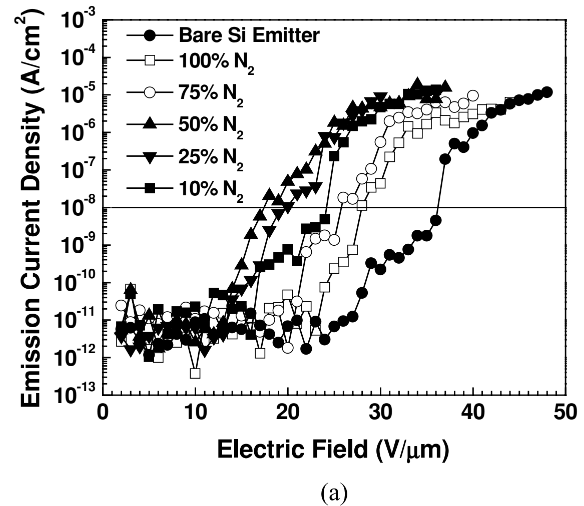


Fig. 4 AES depth profile of a sputtered STO film on Si deposited at 600°C in Ar-10%N_2

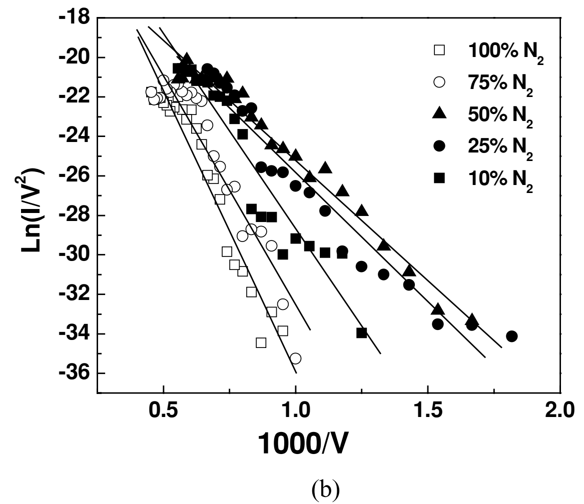
illustrate the substitution of nitrogen in STO perovskite lattice. Moreover, the presence of STO LO phonon mode means that the nucleus formed in 30-nm-thick films are also crystallized. The LO phonon mode can be enhanced with nitrogen incorporation. But this enhancement is limited by certain nitrogen concentration in the lattice, and it will be weakened if the film deposited in the ambient with nitrogen content over 50%. Furthermore, we performed AES depth profile of sputtered STO films to illustrate the nitrogen incorporation in the films during the deposition process. As shown in Fig. 4, the presence of nitrogen is clearly demonstrated in the films deposited in 10% N_2 ambient.

3.2 Influence of sputtering ambient on the field emission of STO coated Si FEAs

Figure 5(a) illustrates the influence of sputtering ambient on the electron emission behavior of Si FEAs coated with 30-nm-thick STO films. The films were deposited at



(a)



(b)

Fig. 5 Electron emission characteristics (a) and F-N plots (b) of 30-nm-thick STO films on Si FEAs deposited at 600°C in different nitrogen content ambient

1.6×10^{-2} mbar with nitrogen contents from 10% to 100%. Meanwhile, electron emission characteristic of bare Si FEAs is also plotted for comparison. It is shown that the threshold field of electron emission is highly correlated to the nitrogen content in the sputtering ambient. With the increase of nitrogen content, the threshold field is lowered tremendously from 36.24 V/μm for bare Si FEAs to 17.4 V/μm for STO-coated FEAs deposited in 50% N_2 ambient. However, further increasing nitrogen content does not lead to further improvement in electron emission behavior. The threshold field measured is about 25.8 and 28.0 V/μm for the films deposited in 75% and 100% N_2 ambient respectively.

The Flowler-Nordhiem (F-N) equation is applied to characterize the emission data of STO-coated Si FEAs,

$$I = aV^2 \exp(-b\phi^{3/2}/V) \tag{1}$$

Table 1 FNSL parameters and effective work function of 30-nm-thick STO coated Si FEAs as a function of nitrogen content in sputtering gas

Nitrogen content in sputtering gas (%)	Thickness of STO film (nm)	$FNSL_{STO}/FNSL_{Si}$	Φ_{STO} (eV)
10	30	0.5918	2.89
25	30	0.3914	2.19
50	30	0.3642	2.09
75	30	0.6940	3.21
100	30	0.8514	3.68

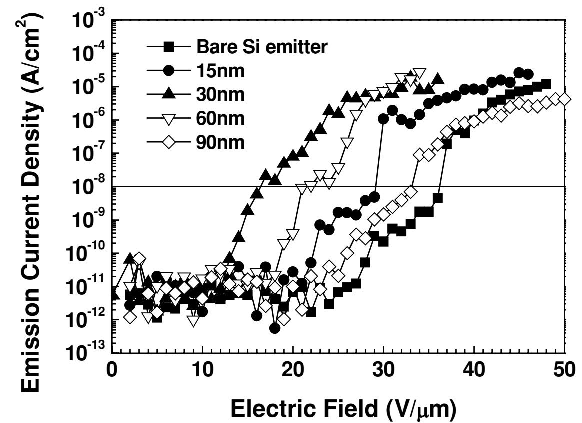
where a and b are constant, I is the emission current, and ϕ is the work function of the emitting surface. The measured emission current conforms to F-N behavior with a linear $\ln(I/V^2)$ versus $1/E$ plot as shown in Fig. 5(b). According to the F-N slope and Si work function of 4.1 eV, the effective work function of STO-coated tips can be deduced by

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

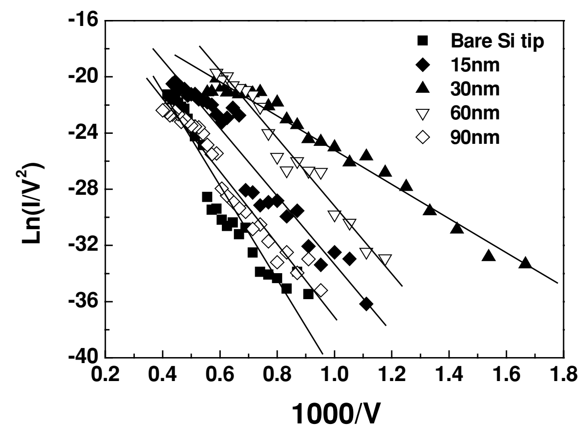
where $FNSL$ is the slope of F-N plot. Table 1 lists estimated effective work function from F-N slopes, and the lowest value is achieved in the film deposited in 50% N_2 ambient. To correlate with our XRD and FTIR studies mentioned above, the film deposited in 50% N_2 ambient exhibits the enhanced crystallinity owing to the incorporation of nitrogen. The substitution of nitrogen for oxygen would result in band-gap narrowing owing to the formation of N_{2p} band which is located above the O_{2p} valence band [5]. As a result, the film deposited in 50% N_2 ambient demonstrates better electron emission behavior with lowered effective work function.

3.3 Influence of thickness on the field emission of STO coated Si FEAs

Figure 6(a) illustrates the influence of STO film thickness on the electron emission behavior of coated Si FEAs. The films were deposited in 50% N_2 ambient at 600°C with thickness from 15 nm to 90 nm. It is shown that the threshold field of electron emission is lowered tremendously from 36.24 V/μm for bare Si FEAs to 17.34 V/μm for the surface modified FEAs with 30-nm-thick STO coating. However, further increasing STO thickness would deteriorate the electron emission characteristics of Si FEAs. Similarly, the measured emission current also conforms to F-N behavior with a linear $\ln(I/V^2)$ versus $1/E$ plot as shown in Fig. 6(b). Table 2 lists the estimated effective work function of these FEAs from F-N slop. The FEAs coated 30-nm-thick STO exhibit the lowest effective work function. It is believed that the dependence of film thickness might be related to the so-called space-charge-induced band-bending interlayer at STO/Si interface, which is similar to that in amorphous carbon thin films proposed by Silva [9]. The band-bending occurs as a result of carrier depletion across the whole thickness of STO film, which gives rise to a maximum internal electric field close to the heterojunction. Therefore, there is an optimum thickness for lower threshold electron emission. If the film is too thick, the STO films would not be fully depleted, and therefore, the energy loss of the hot electrons would be large and thus prevent it from escaping from the surface. If the film is too thin, electrons that are emitted from the heterojunction will not gain



(a)



(b)

Fig. 6 Electron emission characteristics (a) and F-N plots (b) of sputtered STO films on Si FEAs with thickness from 15 nm to 90 nm, deposited at 600°C in Ar-50%N_2 ambient

Table 2 FNSL parameters and effective work function of STO-coated Si FEAs as a function of STO thickness. The STO films were deposited in Ar-50%N_2 ambient at 600°C

Nitrogen content in sputtering gas (%)	Thickness of STO film (nm)	$FNSL_{STO}/FNSL_{Si}$	Φ_{STO} (eV)
50	15	0.7247	3.31
50	30	0.3642	2.09
50	60	0.7225	3.30
50	90	0.7753	3.46

enough energy relative to the conduction band for them to be able to surmount the emission barrier to vacuum.

4 Conclusion

Nitrogen doped STO films have been fabricated on Si FEAs using reactive RF magnetron sputtering for electron emission applications. FTIR and AES results reveal that nitrogen has been successfully incorporated in STO films while sputtered in Ar-N_2 mixture ambient. Low dose incorporation of nitrogen shows enhanced crystallinity in STO films. However, the perovskite structure would be deteriorated in nitrogen-overdosed films, which are deposited in the higher nitrogen content ambient, and hence the degraded XRD patterns and FTIR spectra are shown. Electron emission characteristics of STO-coated Si FEAs are highly correlated with the nitrogen content in sputtering gas. The threshold field is lowered tremendously from 36.24 V/μm for uncoated FEAs to 17.37 V/μm for 30-nm-STO coated FEAs deposited in 50% N_2 ambient. The work function of emitter surface is also reduced from 4.1 eV to 2.09 eV correspondingly. The enhanced electron emission is believed to originate from the band-gap narrowing in STO owing to the substitution of nitrogen for oxygen. Meanwhile, the electron emission characteristic is also dependent on the thickness of STO coating. The thickness dependence might be related to the so-called space-charge-induced band-bending interlayer at STO/Si interface, which occurs as a result of carrier depletion across the whole thickness of STO film.

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