Tunable superconductivity of epitaxial TiN films through oxygen doping

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ABSTRACT
Titanium nitride (TiN) film is a remarkable material for a variety of applications ranging from superhard coating to superconducting quantum devices, which can be easily oxidized when it works in the atmosphere. However, the study of its oxidation effect on the crystal and electronic structures of epitaxial TiN films is rare as yet. Here, we coherently synthesize TiN epitaxial films on MgO single crystal substrates via reactive magnetron sputtering and, then, dope oxygen into these films via a controllable oxidation process. The crystal and electronic structures are characterized by high-resolution x-ray diffraction, x-ray photoelectron spectra, and Raman spectra. It is revealed that the crystal structure remains to be of the rocksalt type in these films even with heavy oxygen doping. The data of temperature-dependent electrical transport measurements indicate that the superconducting critical temperature (kinetic inductance) decreases (increases) from 4.6 K (0.672 pH/\(\square\)) in the pristine TiN film to 3.4 K (1.13 pH/\(\square\)) in the film with a maximum oxygen doping level. Our work provides a controllable way to tune the superconductivity of TiN films, which enables the flexibility to engineer the resultant performance of TiN-based superconducting quantum devices.

I. INTRODUCTION
Due to its excellent mechanical robustness, highly tunable plasma frequency, and good compatibility with semiconductors, TiN film is a remarkable material for various applications such as decorative and wear-resistant coating, plasmonic devices, and integrated circuits. In particular, owing to high kinetic inductance (KI) and low dielectric loss in the superconducting state, TiN films are promising candidates for single photon detectors, superconducting phase shifters, ultra-sensitive current sensors, low loss coplanar waveguide resonators, and quantum-information processing devices. Despite wide applications, TiN can be easily oxidized under ambient conditions, which makes the study of oxidized TiN very important and intriguing from application perspectives.

Previously, deep understanding of oxidation kinetics and mechanisms had been well-established for TiN in the form of ceramics, nanocrystals, and polycrystalline films, and these oxidized TiN films have been widely exploited for numerous applications, including coatings, catalysts, and supercapacitors. However, the study of oxidized TiN epitaxial films with high crystalline quality has received much less research attention. Wu et al. found anatase formation in the oxidation process of the TiN epitaxial film. Moatti et al. reported the formation of a rutile TiO\(_2\) epitaxial layer through oxidation of TiN(100)/Si(100) thin films. Additionally, as for superconductivity, doping has been proved to be a powerful
method. So far, apart from several investigations on the superconductivity of TiN with unintended oxygen doping, a comprehensive study of the doping effect on the superconductivity using a controllable oxidation method in the highly epitaxial TiN film is rare.

Here, we report an oxygen doping effect on the properties of highly epitaxial TiN films via a controllable oxidation process. Surface chemical compositions of the oxidized films are analyzed by x-ray photoelectron spectra (XPS). It is indicated that the ratio of Ti\(^{4+}/\)Ti\(^{3+}\) increases with increasing oxidation temperature. Despite the high concentration of Ti\(^{4+}\) cations on the surface, the overall structure remains to be of the rocksalt-type, and the out-of-plane lattice constant decreases with more oxygen content, which are evidenced from high-resolution x-ray diffractometry and Raman spectroscopy investigations. The low-temperature electrical transport measurements reveal that the superconducting critical temperature (kinetic inductance) decreases (increases) from 4.6 K (0.672 pH/\(\Box\)) in pristine TiN films to 3.4 K (1.13 pH/\(\Box\)) in the highest oxygen doped films. Our work provides a novel way to tune the superconductivity of TiN films, which enables the flexibility to engineer the resultant performance of TiN-based superconducting devices.

II. EXPERIMENT

TiN possesses a cubic rocksalt structure with the lattice parameter \(a = 4.244 \text{ Å}\) [see Fig. 1(a)]. To synthesize oxidized TiN (TiO\(_x\)N\(_y\)) films, a two-step method was applied, as shown in Fig. 1(b). First, TiN films of high quality were synthesized on MgO (001) single crystal substrates (10 \(\times\) 10 \(\times\) 0.5 mm\(^3\)) by radio frequency (RF) reactive magnetron sputtering (customized, AdNaNotek) using 2 in. Ti (purity of 99.995%) target and N\(_2\) (purity of 99.999%) reactive gas [see Fig. 1(b)]. During growth, N\(_2\) pressure was kept at 0.02 Torr with a gas flow of 3.2 sccm, and the substrate temperature was held at 800°C. The power of the RF generator was 100 W. After 5 h of deposition (thickness \(\sim\)80 nm), the samples were cooled down to room temperature in the same N\(_2\) atmosphere. Then, the TiN films were cut into four pieces with an even size of 5 \(\times\) 5 \(\times\) 0.5 mm\(^3\). One piece was assigned as the pristine sample without further processing, and the other three pieces were oxidized at 400°C, 500°C, and 600°C for 1 h under 0.02 Torr oxygen pressure with a gas flow of 3.2 scmc [see Fig. 1(b)]. These oxygen-annealed (OA) samples were labeled OA400, OA500, and OA600. The microstructures of all films were characterized by 2θ-ω scanning and Reciprocal Space Mapping (RSM) on a Bruker D8 high-definition x-ray diffractometer using monochromatic Cu K\(_{\alpha1}\) radiation with a wavelength of 1.5406 Å. The chemical compositions were detected by PHI 5000 Versa Probe x-ray photoelectron spectroscopy (XPS) at acceptance angles of 60° for the analyzer. The electrical properties were measured using the physical property measurement system (PPMS from Quantum Design) with four-point probe measurements.

III. RESULTS AND DISCUSSION

The single crystallinity of the pristine TiN films was investigated by wide-range 2θ-ω scan and reciprocal space mapping around MgO (001) diffraction shown in Figs. 1(c) and 1(d). Apart from (002) diffraction peaks of TiN and MgO, no secondary phase is observed in the 2θ-ω scan. It is noted that both bulk TiN and MgO hold a rocksalt crystal structure, and their lattice mismatch is very small (<0.66% with \(a = 4.216 \text{ Å}\) in MgO). Therefore, the TiN films
were coherently grown on the MgO substrate with the out-of-plane lattice parameter of \( c = 4.250 \) Å calculated from RSM, as shown in Fig. 1(d). After oxidation, the colors of TiN films gradually transform from gold in the pristine sample to orange in the OA600 sample [see Fig. 1(b)]. This color variation indicates possible changes in the band structure due to the partial replacement of N atoms by O atoms, which is consistent with previous reports.  

Since the superconductivity in the TiN film is quite sensitive to the chemical compositions,

\[ \text{we performed XPS measurements on all samples [see Fig. 2(a)]. In addition, the XPS spectrum from the pristine sample after etching by Ar ions is also presented as a reference. It is clear that the surface layer of the pristine sample can be easily oxidized under ambient conditions as evidenced by the \( 2p_{3/2} \) signals of Ti\(^{3+} \) (458.3 eV) and Ti\(^{4+} \) (456.6 eV), which is common for TiN films.} \]

\[ \text{According to the report from Shah et al., the features of Ti\(^{3+} \) and Ti\(^{4+} \), here, can be assigned to Ti–O and Ti–N–O bonds corresponding to TiO}_2 \text{ and TiO}_x \text{N}_y, respectively.}\]

\[ \text{After etching, these features disappear. Apart from Ti\(^{3+} \) (454.9 eV), a small amount of Ti\(^{2+} \) (453.0 eV) is found in the etched sample, which might result from nitrogen vacancies.} \]

\[ \text{Oxidation can significantly change the chemical composition of the surface layer as revealed by Fig. 2(b). The content of Ti\(^{3+} \) increases (Ti\(^{3+} \) decreases) with the increase in the oxidation temperature, indicating that more Ti\(^{3+} \) cations are oxidized into Ti\(^{4+} \) cations. Almost all Ti\(^{3+} \) cations in the surface layer are oxidized into Ti\(^{3+} \) cations at around 600 °C. Similar variations in Ti\(^{3+} \) and Ti\(^{4+} \) core level peaks with the increase in the oxidation temperature were also reported by Esaka et al. 35 They proposed that an N\(_x\)-Ti-O\(_y\)–like structure forms through the diffusion of O atoms into the TiN lattice at the initial stage of oxidation before complete transformation of the surface layer into TiO\(_2\). This means there should be a TiO\(_2\) surface layer on the highly oxidized TiN films.}\]

To reveal the structure beneath the surface layer, we conduct zoom-in \( \theta-\omega \) scanning and Raman spectra measurements.

Surprisingly, despite the high concentration of Ti\(^{4+} \) cations at sample surfaces, the oxidized TiN films remain highly (001)-oriented, as shown in Fig. 3(a). The above phenomenon suggests the formation of TiO\(_x\)N\(_y\) with a rocksalt structure due to the partial replacement of N atoms by O atoms. The formation of TiO\(_x\)N\(_y\) can also be supported by the gradual shift of (002) diffraction peaks toward high diffraction angles as in the oxidation temperature increases. The shift indicates the shrinkage of the out-of-plane lattice parameters due to more replacements of N atoms by O atoms with smaller ionic radius. 35 Since signals from the MgO substrate can be seen above the wavenumber of 1000 cm\(^{-1}\), the Raman spectra shown in Fig. 3(b) can reveal the overall structure of all films. All oxidized TiN films present essentially the same Raman active modes as those in the pristine TiN sample, regardless of the relative shift of certain modes. Even for highly oxidized sample like OA600, no conspicuous signals from rutile TiO\(_2\) or anatase TiO\(_2\) can be observed, implying that the surface layer with a high concentration of Ti\(^{4+} \) cations could be too thin to be probed. 35 Due to the octahedral symmetry breaking by the point defects, e.g., nitrogen vacancies, first-order modes including transverse acoustic mode (TA, 215 cm\(^{-1}\)) and longitudinal acoustic mode (LA, 313 cm\(^{-1}\)) side from high wavenumber second-order acoustic and optical modes (2TA, TO, 2LA, and A + O) can be clearly seen in the pristine TiN film. 35 The red shift for TA and TO modes, blue shift for 2TA modes, and continuous variations in relative intensities for modes like LA and 2TA with increasing oxidation temperatures suggest changes in the microstructure, e.g., film strain, brought by more replacement of N by O after oxidation. Further study will be needed to clarify the mechanism behind the oxidation origin of mode variations observed in the Raman spectra. Nevertheless, the oxidized TiN (TiO\(_x\)N\(_y\)) samples holding an overall rocksalt structure are indisputable from zoom-in \( \theta-\omega \) scanning and Raman spectroscopy investigations. Therefore, the oxidation process induces an oxygen doping effect on the highly epitaxial TiN films, and the
oxygen doping level increases with the increase in the oxidation temperature.

Finally, we discuss the effect of oxygen doping on the superconductivity of TiN films. As shown in Fig. 4(a), the sharp transition from the normal state to the superconducting state can be clearly seen for all films. The resistivity $\rho_N$ in the normal metal state (measured just above $T_c$) of 17.3 $\mu\Omega$ cm and $T_c$ of 4.6 K in the OA400 sample are very close to those in pristine TiN samples, which suggests barely detectable changes in superconductivity upon slight oxygen doping with 400 $^\circ$C annealing. However, further increase
in the oxygen doping level with higher annealing temperature significantly change both normal metal and superconducting states. $\rho_N$ rises from 18.9 $\mu\Omega$ cm in the OA500 sample to 23.6 $\mu\Omega$ cm in the OA600 sample, while $T_c$ drops from 4.4 K in the OA500 sample to 3.6 K in the OA600 sample. The impact of oxygen doping on superconductivity can also be inspected from the 2 K magnetoresistance shown in Fig. 4(b). The critical magnetic field $H_c$ for pristine, OA400, OA500, and OA600 samples are 0.4 T, 0.40 T, 0.35 T, and 0.20 T, respectively. We propose several mechanisms of this kind of enhanced $\rho_N$ and suppressed $T_c$ and $H_c$ in the heavily oxygen doped films. First, cubic TiO$_N$ can be regarded as solid solutions of TiO and TiN with possible defects.\textsuperscript{37,38} Cubic TiO is superconducting with typical $T_c$ lower than 2 K.\textsuperscript{11} Increasing oxygen content in TiO$_N$, via high oxidation temperature annealing will naturally lead to suppressed superconductivity. Additionally, the increasing anion disorder via the partial replacement of N by O and other defects can also contribute to the suppressed superconductivity.\textsuperscript{20,51} Last, the highly oxidized surface layer of TiN films can present weak magnetic disorder, which could increase the scattering probability for carriers and shorten the superconducting coherence time.\textsuperscript{25} The $L_0$ of all films are also evaluated by using the equation $L_0 = \frac{\hbar R_0}{\pi \Delta_0}$, where $R_0 = \rho_N / t$ is the sheet resistance of the normal metal state and $\Delta_0 = 1.76k_B T_c$ is the superconducting energy gap.\textsuperscript{12,44} Then, the calculated $L_0$ for all films are listed in Table I. As can be seen in Fig. 4(c), $L_0$ increases from 0.672 pH/$\Omega$ in pristine TiN to 1.13 pH/$\Omega$ in OA600, almost doubled in the film with the highest oxygen doping level.

### IV. CONCLUSION

In conclusion, we synthesize a series of epitaxial TiO$_N$$_y$ films based on high quality epitaxial TiN films with a controllable oxygen doping process. Their structural and electrical properties are characterized by XRD, Raman, XPS, and PPMS measurements. The XRD and Raman data confirm an invariable rocksalt structure for the TiO$_N$$_y$ films and shrinkage of the out-of-plane lattice constant with high oxygen doping level, despite high concentration of Ti$^{4+}$ ions on the surface layer as evidenced by the XPS investigations. PPMS measurements reveal that the superconductivity can be effectively controlled by the oxygen dopant. Superconducting $T_c$ (kinetic inductance) decreases (increases) from 4.6 K (0.672 pH/$\Omega$) in pristine TiN films to 3.4 K (1.13 pH/$\Omega$) in the heaviest oxygen doped films. This tunable superconductivity could be attributed to the suppressed superconductivity in TiO, increased anion disorder, and weak magnetic disorder. Our work demonstrates that this controllable oxidation process is a powerful way to tune the properties of highly epitaxial TiN films after deposition, which offers flexibility to adjust the resultant performance of TiN-based superconducting quantum devices.

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