Ultrathin epitaxial superconducting niobium nitride films grown by a chemical solution technique†

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Ultrathin epitaxial superconducting NbN (18 nm) films, exhibiting a superconducting transition temperature of 14 K and a critical current density as high as 5.2 MA cm^{-2} at 5 K under zero magnetic field, were grown on $SrTiO_3$ (STO) by a chemical solution technique, polymer assisted deposition (PAD).

Niobium nitride (NbN) is a well-known superconductor and has been considered to be one of the promising cryoelectronic materials.[1] For example, its relatively high transition temperature, large superconducting energy gap, good thermal cyclability, and ease of fabrication make it a promising junction electrode material. NbN has been used to fabricate superconductor/insulator/superconductor tunnel junctions receivers operating at submillimeter wave ranges.[1,2] For these applications, it is necessary to grow epitaxial NbN films. There have been some reports on the preparation and properties of NbN films fabricated by reactive sputtering,[3] vapor deposition,[4] pulsed laser deposition,[5] and molecular beam epitaxy.[6] In addition, ultrathin NbN films have also found applications in optical communication and quantum information technologies. For instance, the superconducting single photon detector (SSPD) based on ultrathin NbN films can be very fast and sensitive to detect both visible and infrared photons.[7] Other applications such as superconducting hot electron bolometer (HEB) mixers for high-resolution spectroscopy at frequencies between 1.5 and 6 THz also require highly crystalline ultrathin films with high performance superconducting properties. These applications highlight the interest in the development of new low cost, relatively simple techniques to produce high quality, ultrathin superconducting NbN films. In general, most hetero-epitaxial NbN films had traditionally been grown on matched lattice substrates such as MgO and semiconductors with the help of buffer layers. However, lattice mismatch between the substrate many times has a significant impact on device performance. For example, lattice mismatch of more than 10% between the film and the substrate is helpful for SSPDs.[8] Of course it is often difficult to get high quality epitaxy on substrates with large lattice mismatches. One of the challenges in these systems is to enable the growth of ultrathin epitaxial NbN films on the substrates with large lattice mismatch.

In the present work, we have employed a chemical solution deposition technique, polymer-assisted deposition (PAD), to grow ultrathin epitaxial NbN films on $SrTiO_3$ (STO) substrate (with lattice mismatch as high as 12.6%). Chemical solution deposition for the growth of thin films provides advantages such as low cost, easy setup, and large area coating. We have recently demonstrated that PAD based on a solution approach is a very promising technique to grow epitaxial complex metal-oxide thin films.[9] In this process, the soluble polymer plays a significant role in preparing high quality metal oxide films. In other words, the polymer not only controls the desired viscosity for the process, but also binds the metal ions to prevent premature precipitation and formation of metal oligomers. The results are a homogeneous distribution of the metal precursors in the solution and the formation of uniform metal oxide films. In this paper, we report our efforts to grow very thin epitaxial NbN films on STO substrate by PAD technique (see ESI for details).† To the best of our knowledge, this is the first report for the epitaxial NbN films grown on STO substrate.

Fig. 1 shows the X-ray diffraction (XRD) patterns (θ–2θ scan, rocking curve, and phi (ϕ) scans) of the NbN/STO film. As can be seen from the θ–2θ scan in Fig. 1a, there are only (002) peaks from NbN film and STO substrate. The appearance of only (002) peak of the film indicates that the NbN is preferentially oriented along the *c*-axis perpendicular to the substrate surface. It should be noted that no other detectable phases were observed. A value of 1.5° for the full width at

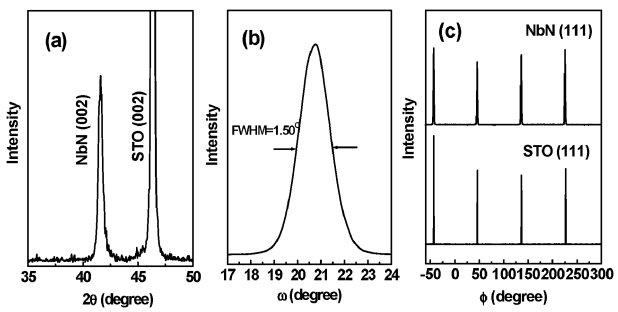

Fig. 1 XRD patterns of a NbN film on a STO substrate. (a) θ–2θ scan; (b) rocking curve from (002); and (c) ϕ-scans from (111) reflections of both the substrate and the film.

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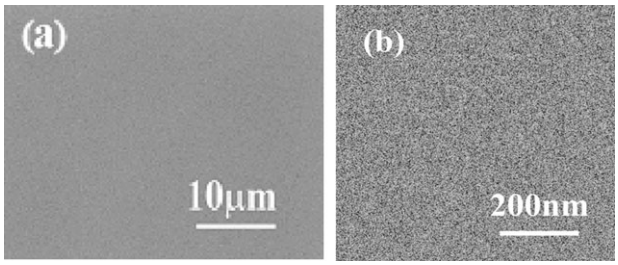

Fig. 2 Surface morphology of an epitaxial NbN film on a STO substrate.

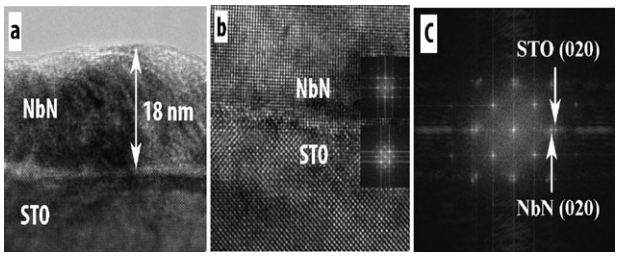

Fig. 3 Interface microstructure between the epitaxial NbN film and STO substrate: (a) a low magnification image of transmission electron microscopy; (b) HRTEM image of the interface (insets presenting FFTs of NbN and STO); (c) the fast Fourier transform (FFT) of the interface.

half-maximum (FWHM) of the rocking curve (Fig. 1b) of (002) NbN reflection, in comparison with a value of 0.2° for the single-crystalline STO substrate, indicates good crystallinity of the films. The in-plane orientation between the film and the substrate was determined by XRD ϕ-scans from (111) NbN and (111) STO, respectively. As shown in Fig. 1c, the film is well aligned in-plane with the substrate. The epitaxial quality is quite good, considering the lattice mismatch since the average FWHM value is 1.6° for the NbN film, as compared to a value of 0.5° for the STO substrate. The hetero-epitaxial relationships between the NbN film and STO substrate, based on Fig. 1a and 1c, can be described as (001)NbN||(001)STO and [111]NbN||[111]STO. Such epitaxial relationships can be understood by considering the basal plane lattice constants of NbN (a = 0.439 nm) and STO (a = 0.39 nm). It is noted that the lattice mismatch between the NbN and the STO is as high as 12.6%. Our experimental results demonstrate that PAD route provides an alternative approach for the preparation of epitaxial films on substrates with large lattice mismatch.

The surface morphologies of the NbN film are shown in Fig. 2. As can be seen from the SEM images of different magnifications (Fig. 2a, b), the film is dense, smooth, and uniform without any detectable cracks or voids. Fig. 3 shows the cross-sectional high-resolution transmission electron micro scopy (HRTEM) image and fast Fourier transform (FFT) patterns taken from different regions. There is an obvious interface between NbN film and STO substrate (Fig. 3a). The thickness of the film prepared using our process is about 18 nm.

The HRTEM image in Fig. 3b shows the clear and dense film and substrate without the presence of any other phases.

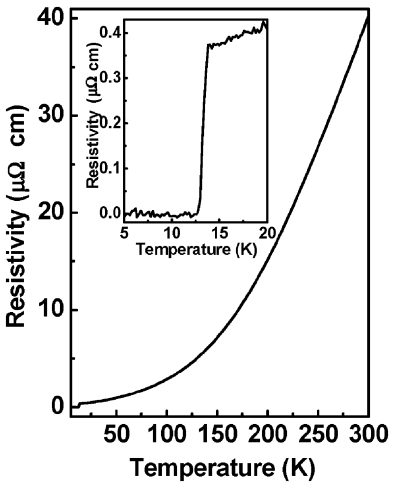

Fig. 4 Temperature dependent resistivity of an epitaxial NbN film on a STO substrate. The inset displays an enlarged temperature dependent resistivity from 5 to 20 K.

The clear patterns present the high crystallinity of the NbN films. Insets in Fig. 3b represent the corresponding FFT of film (top) and substrate (below). Moreover, the FFTs of the interface between NbN and STO exhibit two distinct sets of patterns in Fig. 3c. We would like to point out that the corresponding FFT patterns show the same epitaxial relationship between the NbN film and the STO substrate as deduced from XRD analysis. The lattice parameter of such epitaxial NbN film calculated from the HRTEM is 0.432 nm which is in agreement with a value of 0.435 nm calculated from the X-ray diffraction measurement. The same lattice constants (within the measurement error) between the bulk and the film indicate that our epitaxial NbN film is relaxed.

Our epitaxial NbN film exhibits the desired superconducting properties. Fig. 4 shows the plots of resistivity *vs.* temperature of the epitaxial NbN film. The resistivity increases with the temperature from 14 to 300 K, a metallic behavior commonly observed for high quality NbN film. The inset in Fig. 4 shows resistivity *vs.* temperature from 5 to 20 K. It is clearly seen that there is a superconducting transition at a temperature of 14 K. To the best of our knowledge, we have also obtained the lowest normal-state resistivity at 20 K ($\rho_{20\ K}$ = 0.41 μΩ cm) and the largest residual resistivity ratio of 98.4, defined as RRR = $\rho_{300\ K}/\rho_{20\ K}$.[10] These results further indicate the epitaxial NbN films' high crystallinity.

Fig. 5 displays the magnetization *vs.* temperature and magnetic field, respectively. A superconductive transition at a temperature of 14 K was also observed in these measurements. This transition temperature is the same as that observed in resistivity *vs.* temperature measurement. In addition, the critical current density (J_c) deduced from the field dependent magnetization (shown in Fig. 5b) is about 5.2 MA cm^{-2} at 5 K, which suggests that this epitaxial film has potential for electronic device applications, such as microwave device and superconducting quantum interference devices. It also illustrates the high quality of these superconducting films.

In summary, ultrathin epitaxial superconducting NbN films have been successfully grown on STO substrates by a polymer

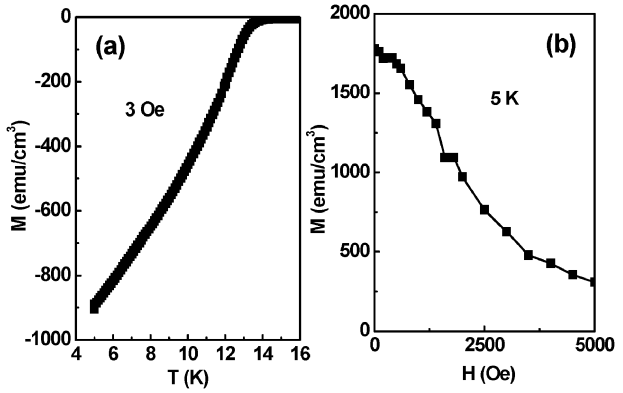

Fig. 5 Magnetization *vs.* temperature (a) and magnetic field (b) of an epitaxial NbN film on a STO substrate, respectively.

assisted deposition technique. The structure of the NbN films has been examined by XRD and electronic microscopy. The epitaxial relationships between the film and substrate can be described as (001)NbN||(001)STO and [111]NbN||[111]STO. The films show a transition temperature of 14 K and a critical current density (J_c) of 5.2 MA cm^{-2} at 5 K under zero magnetic field. All the results suggest this expitaxial film has potential for electronic device applications.

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