



The influence of nitrogen pressure on formation of niobium nitride by thermal processing

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ABSTRACT

The nitridation of niobium by thermal processing at 1300 °C in different nitrogen (N₂) gas pressures ranging from 2.6×10^{-4} to 3.3×10^0 Pa was investigated. The NbN_x films were grown on the niobium substrate by reactive thermal heating. The effect of nitrogen background pressure on the structure and morphology of the formed NbN_x phase was studied by X-ray diffraction (XRD) and atomic force microscopy (AFM). The electronic structure of the NbN_x films was investigated by X-ray absorption near edge structure (XANES). The phase formation followed a sequence of α -Nb(N) → β -Nb₂N when the nitrogen pressure was increased. As the pressure was increased to $>1.3 \times 10^{-3}$ Pa, the nitride film develop into the α -Nb(N) phase mixed with the β -Nb₂N phase. Increasing nitrogen pressure results in more β -phase concentration accompanied by an increase of other phases. Higher pressure promotes the diffusion of adsorbed nitrogen, and consequently the formation of different phases of NbN_x. The diffusion of nitrogen in the Nb surface and its reactivity governs the phase formation of NbN_x. XANES measurements at the Nb M-edge showed strong hybridizations between the Nb 4d and N 2p states due to larger covalent contribution to the Nb–N bonding. On the basis of these observations our density of state calculation revealed that presence of the β -Nb₂N phase in NbN_x results in a large covalent contribution than that by the α -NbN phase.

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1. Introduction

Transition metal nitrides possesses an unusual combination of electronic and mechanical properties, which make them attractive for technological applications. In recent years, significant attention has been paid to the study of niobium nitride (NbN_x), which exhibits unique properties that makes it attractive for many technical and industrial applications. For instance, niobium nitride has high hardness and wear resistance, high superconducting transition temperature (T_c), and excellent thermal and chemical stabilities [1–4]. Niobium nitride thin films are of interest as they can be used for gas sensors, diffusion barriers in Josephson junctions, cathode

materials in vacuum microelectronic devices, and coatings for superconducting cables [5–7]. NbN_x coatings on Nb show an increase in the surface hardness as well as they provide a barrier layer for the hydrogen diffusion into Nb for applications in superconducting radiofrequency cavities. NbN_x crystallize in different phases, including β -Nb₂N (hexagonal), γ -Nb₄N₃ (tetragonal) δ -NbN (face-centered cubic), δ' -NbN (hexagonal), ϵ -NbN (hexagonal), and the η -NbN (hexagonal) structure. The diffusion of nitrogen onto the niobium surface occurs by heating a niobium substrate at high temperatures in a background of nitrogen gas. Reactions between the diffused nitrogen with niobium occurs forming nitrides [8–12]. Combustion synthesis is another method used to form NbN_x [13]. NbN_x thin films were also produced by rapid thermal processing of Nb thin films, deposited on Si, in a background of molecular nitrogen or ammonia [14,15]. In general, these methods depend on adsorption of nitrogen or ammonia on the surface of niobium that is heated at high temperatures. Treatment of Nb samples at different heating temperatures or background pressures results in

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the formation of different NbN_x phases, stoichiometry, and morphology. The reactive diffusion process for NbN_x formation is simple, cheap, and results in uniformly covering larger areas with a homogenous thickness, and is effective in rapid formation of micron-size nitride layers [10,16]. NbN has a critical superconducting transition temperature (T_c) higher than Nb, it is very stable to structural disorder and radiation damage. The phase diagram of the Nb–N system is complicated and includes many different phases [17]. The selection of nitrogen background pressure and substrate temperature affects the phase of the NbN_x coating. Musenich et al., studied the nitride formation in 150 kPa N_2 background pressure in the temperature range 1100–1900 °C [10]. They observed formation of multiphases of NbN_x . Their work mainly focused on the growth kinetics and the mechanism of the reaction between the N_2 gas and Nb. That work, however, did not study the electronic structure of the NbN_x surface layer. We have previously studied NbN_x coatings formed by heating in the range of 1250–1500 °C at 1.3×10^{-3} Pa N_2 background gas pressure [16]. Only the α - NbN phase was detected with no transformation to another NbN_x phases observed. In the present study, we performed a series of experiments to investigate the formation of NbN_x in different background nitrogen gas pressures in the range 2.6×10^{-4} – 3.3×10^0 Pa when heating Nb at 1300 °C. The study focuses on the structural and electronic characterization of NbN_x films formed with various nitrogen background pressures. The effect of the nitrogen gas pressure on the NbN_x phase formed is studied and conditions for the formation of the hexagonal β - Nb_2N phase, which is the hardest of the NbN_x phases [18], are identified.

2. Materials and methods

An ingot Nb substrate of 99.99% purity with dimensions of $8 \times 3 \times 0.2 \text{ mm}^3$ was used. The substrate was mounted on a tungsten sample holder, which can resistively heat the sample up to 1500 °C. Standard buffered chemical polishing (BCP) method was used for cleaning the Nb substrate. The substrate was mounted in an ultrahigh vacuum (UHV) chamber pumped by a turbomolecular pump and an ion pump to a background pressure in the low 1.3×10^{-4} Pa. The Nb substrate was kept at 700 °C during the chamber bakeout. For nitridation, ultrahigh pure nitrogen (99.999%) was introduced into the chamber using a needle valve with the ion pump sealed and the chamber pumper by the 300 l/s turbomolecular pump. The thermal nitridation was done at different nitrogen background pressures ranging from 2.6×10^{-4} to 3.3 Pa at 1300 °C substrate temperature. The substrate temperature was measured using an optical pyrometer (IGA 15 plus, Mikron Infrared Inc.) through a quartz window and controlled by the current applied to the heater. The samples were processed for 180 min. In order to reach the desired pressure, the ion pump was turned off while the valve connecting the ultrahigh vacuum (UHV) chamber to the turbomolecular pump remained closed. Then, the ultrahigh purity nitrogen gas was introduced into the chamber through a variable leak valve to reach desired pressure. At the end of the 180 min nitridation process, the valve connecting the chamber to the turbomolecular pump was opened and the power to the sample heater was simultaneously turned off to allow the sample to cool down in vacuum after pump-down with the turbomolecular pump for 90 min. We used a different Nb substrate for each growth condition. The Nb substrates were all cleaned following the same BCP method.

XRD measurements were done using a Bruker-AXS three-circle diffractometer. The Bruker SMART APEX II instrument is equipped with graphite-monochromated CuK_α radiation and a SMART Apex II CCD detector. The X-ray source of wavelength 1.5406 Å ($\text{CuK}_{\alpha 1}$) is fixed and both the charge coupled device (CCD) detector 2θ and

sample ω are movable. The detector 2θ is covering about 30° per image position. Three image positions were used for the experiment. In each case, the angle 2θ is the center position of the 30° CCD image, and each value is set so that the angles of incidence and diffraction are equal. Two dimensional (2D) XRD images are recorded for each sample.

The X-ray absorption near edge structure (XANES) measurements performed on beamline 8.2 at the Stanford Synchrotron Radiation Lightsource in the SLAC National Accelerator Laboratory. The beamline 8.2 is a bending-magnet beamline dedicated to photoemission, photoabsorption spectroscopy, and XANES experiments within an energy range of 100–1300 eV. The M edge spectra of niobium were measured in total electron yield (TEY) mode. The TEY signal in 3d transition metals is generated by secondary electrons following X-ray photon absorption. TEY spectra were collected at room temperature by measuring the sample current. The current measurements were done using a Stanford Research System low noise preamplifier Model SR570. The beam flux (I_0) signal from a gold grid was used to normalize the spectra. The X-ray incidence angle was controlled by a rotatable manipulator with an accuracy of about 0.2°. The base pressure of the chamber during the experiment was about 2.0×10^{-7} Pa.

3. Results and discussion

3.1. Structure and phase formation

Fig. 1 shows the XRD patterns of NbN_x films prepared by heating the Nb substrate at 1300 °C in different nitrogen pressures for 180 min. The XRD pattern of the Nb substrate is also included in Fig. 1 as a reference.

Fig. 1 indicates that the films are polycrystalline and can be indexed based on the crystal structure of the bcc α - Nb(N) and the hexagonal β - Nb_2N phases [19,20]. The XRD data were fitted by the Material Analysis Using Diffraction (MAUD) program, for Rietveld analysis [21]. The crystal structures and lattice parameters were obtained using the MAUD software.

XRD peaks for samples prepared at 3.3 Pa showed β - Nb_2N mixed

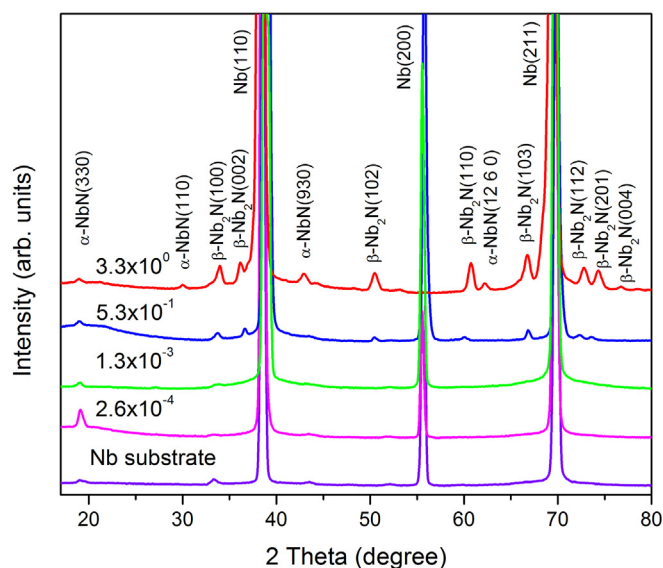


Fig. 1. XRD patterns of NbN_x thin films grown on Nb substrates at 1300 °C temperature in different nitrogen background pressures. The nitrogen pressures in Pascals (Pa) are given at the side of each pattern. The XRD pattern of the Nb substrate is also shown at the bottom.

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