Effects of Heat-treatment on Mechanical Properties and Corrosion Resistance of NbN Films

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Abstract

The NbN and Nb films are prepared by the technique of radio frequency (RF) magnetron sputtering and heat-treated at 300 °C and 400 °C respectively in the present work. The influences of heat-treatment on the morphology, chemical composition, structure, nanomechanical properties and corrosion resistance of the films are studied. Results show that the particles in the films prepared by the above method are all in nano-size. The polygon shaped particles in the Nb films are very thin and small, while the particles in the NbN films prepared under the same condition are pebble-like, larger, and more compact. The nanomechanical properties and corrosion resistance of both the films are improved apparently after the heat-treatment. The corrosion resistance and mechanical properties of NbN film are always better than those of Nb film. The mechanism about the heat-treatment on the property considering the structural evolution is also discussed in this paper.

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Keywords: NbN films; heat-treatment; mechanical property; corrosion resistance; structure

1. Introduction

NbN and Nb are excellent in mechanical properties, electrical properties and chemical properties, playing an important role in the field of mechanics, microelectronics and chemistry (Wang et al., 2006, Han et al., 2004, Cansever, 2008). More and more attention has been given to the application of NbN and Nb, which have great...
development potential. The current researchers, however, mainly focus on the application of Nb in bulk materials (Han et al., 2004, Cansever, 2008, Dueñas et al., 2009, Zhou et al., 2011). Few researches on NbN and Nb films are reported. Due to the influence of the preparation techniques, there always exist residual stresses in the films, which may shorten their service life (Dueñas et al., 2009, Wang et al., 2010, Arima et al., 2009, Ding et al., 2007, Hwang et al., 2005). In order to maintain good mechanical properties, the films should be heat-treated in low temperature before being put into service (Noufi et al., 1985, Yue et al., 2009, Seo et al., 2010, Litteken et al., 2005, Matsue et al., 1996). Therefore, it is of great significance to study the crystalline transformation and the change of mechanical properties and corrosion resistance of NbN and Nb films during low temperature heat-treatment.

In this study, the films of NbN and Nb are prepared by using magnetron sputtering technology, and then heat-treated at low temperature. The morphology and phase structure before and after treatment are examined to analyze the influence of heat-treatment on the nanomechanical properties and corrosion resistance of the films.

2. Experimental methods

The films of NbN and Nb were sputtering deposited on single crystal Si wafers by radio frequency magnetron sputtering system of JGP450-PECVD200. The substrates were grinded and polished, alkaline degreased, and then ultrasonic cleaned with distilled water and ethanol before deposition. A \( J_{60\times3mm} \) sputtering target made of 99.99\% purity Nb as source material was used and the distance between the target and substrates was 70 cm. The Ar was used as sputtering gas.

During the heat-treatment, the samples were first heated to 300°C or 400°C at 0.3 Pa pressure, isothermal treated at 300 °C for 1 h, and then air cooled.

The morphology, phase structure, nanohardness and the elastic modulus of the films were analyzed with field emitting scanning electron microscope (FESEM), X-ray diffraction (XRD) and nanomechanical test system, respectively.

Corrosion resistance measurements of the films were performed using the electrochemical workstation of PARSTAT2273. The packaged samples were soaked in 3.5% NaCl solution for 1 hour before the electrochemical test. The potentiodynamic polarization test was carried out using a three-electrode system. The saturated calomel is of the reference electrode, and the platinum is of the auxiliary electrode. The test samples with effective exposure working area of 1 cm\(^2\) are of the working electrodes. Tests were carried out in the corrosion medium 3.5% NaCl solution at room temperature. The scanning speed is 0.33 mV/s.

3. Results and discussion

3.1. Effects of heat-treatment on morphology, composition and structure of films

Fig. 1 shows the microstructure of Nb and NbN films before and after heat-treatment. It can be seen that the particles in the Nb films are thin and small with the shape of polygon, while the particles in the NbN films prepared under the same condition are pebble-like, larger, and more compact than that in the Nb films. But all of them are of the nano level. After treatment, the surface of the Nb films becomes more compact, and some white particles appeared on the films that are demonstrated to be oxide of Nb by energy dispersive spectrometer (EDS). The particles in the NbN films become thinner after treatment, and there are some micro-cracks emerged in the films. The higher the treated temperature is, the thinner the particles are, and the wider the micro-cracks are.

The X-ray diffraction results of the Nb and NbN films before and after heat-treatment are given in Fig. 2. Where, we can see that the heat-treatment at low temperature has nearly no effect on the crystallographic orientation of the films. However, after the treatment some diffraction peaks of NbO\(_x\) and Nb\(_4\)N\(_3\) appeared in the diffraction spectra of the Nb and NbN films, which indicates that the modification of film surfaces has occurred and multiphase structure appeared because of the chemical reaction between Nb and O, N in the air.
3.2. Effects of heat-treatment on corrosion resistance of films

The electrochemical results of the films before and after heat-treatment are shown in Fig. 3. In which, the passivation in the anode areas of the Nb and NbN films with or without heat-treatment is obvious, indicating that the films both have excellent corrosion resistance. Before heat treatment, the corrosion current density of the Nb film is about 1 order of magnitude higher than that of the NbN film, which means that the NbN film has better corrosion resistance than the Nb film. After treated at 300 °C, the Ecorr of the NbN film increased up to 300 mV, tremendously above the Ecorr of the Nb film. When treated at 400 °C, the Ecorr of the Nb film improved further and the corrosion current density decreased. It indicates that corrosion resistance of the Nb film increased with increasing treated temperature. Whereas, the NbN film treated at 400 °C has lower corrosion resistance compared with that treated at 300 °C. The reason for this phenomenon is that the micro-cracks in the surface of the NbN film were widened when treated at 400 °C, inducing local gap corrosion on the film surface. As for the Nb film, the elevated treating temperature decreased the crystallinity of the Nb film, and increased its compact, which results in a higher corrosion resistance at higher treating temperature.
3.3. Effects of heat-treatment on the nanomechanical properties

The nanoindentation results of the films under different conditions are shown in Fig. 4. It can be seen that, before heat-treatment, the elastic modulus of the Nb and NbN film is almost the same and the nanohardness of the NbN film is slightly higher than that of the Nb film. After treatment, the nanohardness and elastic modulus of both films improved obviously, and the improvement of the NbN film is even more apparent. It is revealed by XRD and SEM results that the films were oxidized during heat-treatment. In the heat-treatment process, the atom structure may reset partly and a large amount of defects such as vacancies and interstitial atoms may emerge in the crystals,
resulting in an increased hardness of the films. Due to the low heat-treated temperature the defects and the atoms can hardly reach a balance, which leads to a large number of dispersion strengthening effects in the films.

4. Conclusion

The nanoscale films of Nb and NbN prepared by RF magnetron sputtering have compact structure, good nanomechanical property and corrosion resistance. The morphology and phase structure changed obviously during low temperature heat-treatment. The corrosion resistance and nanomechanical property of both films are improved apparently after heat-treatment since the content of nitride and oxide in the film increased in the heat-treatment process.

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