Transport Properties
of Nitrided VN–SiO$_2$ Sol–Gel Derived Films

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This work presents transport properties of $x$VN–(100–$x$)SiO$_2$ (where $x = 90, 80, 70, 60$ mol%) films. The films were prepared by thermal nitridation of sol–gel derived V$_2$O$_5$–SiO$_2$ (in proper molar ratio) coatings. The coatings obtained by sol–gel method are especially suitable for the ammonolysis because of their porosity. The microporous structure allows both a significant incorporation of nitrogen and its distribution through the film. The nitridation process of V$_2$O$_5$–SiO$_2$ coatings leads to the formation of disordered structures, with VN metallic grains dispersed in the matrix of insulating SiO$_2$. The critical temperatures of the superconducting transition of the samples $T_{c, max}$ are about 7.5 K.

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1. Introduction

The vanadium nitride has long been of interest due to its unusual physical properties, which are of technological as well as fundamental importance. From technological point of view, because of its good selectivity and stability [1, 2], VN is an important industrial catalyst. Moreover VN is a superconductor with a transition temperature $\approx 9$ K [3, 4] and may be used in several superconducting microelectronics applications. From a fundamental perspective the focus is to examine the effect of disorder on the electrical and superconducting properties.

Thin films consisting of VN are usually prepared by magnetron sputtering method, physical or chemical vapor deposition and by heating vanadium metal in a nitrogen atmosphere at high temperature. The films presented in this work are prepared by thermal nitridation (with ammonia) of sol–gel derived metal–oxide films [5]. The microporous structure of the films prepared by sol–gel method allows both a significant incorporation of nitrogen and its distribution through the film. This is a very promising method of films preparation, because it gives the possibility to prepare films of any shape and size. As the result of ammonolysis of V$_2$O$_5$–SiO$_2$ coatings, disordered structure with VN metallic grains dispersed in the matrix of insulating SiO$_2$ is obtained.

2. Experimental

The films with a composition $x$VN–(100–$x$)SiO$_2$ (where $x = 90, 80, 70$ and $60$ mol%) were obtained by thermal nitridation of V$_2$O$_5$–SiO$_2$ sol–gel derived films (in a proper V$_2$O$_5$/SiO$_2$ ratio) with ammonia. The starting solution was prepared by mixing tetraethoxysilane (TEOS, 98%) from Fluka and vanadium (V) oxytripropoxide (98%) from Aldrich with ethanol and acetylacetone as the complexing agent. The green color of the as prepared solution was caused by V$^{3+}$ species. The films were deposited on the silica glass substrate by a spin coating technique at a rate of 100 rps, then aged and heated at 250$^\circ$C for 1 hour. Repeating the above procedure three times gave approximately 450 nm thick films. To obtain VN–SiO$_2$ coatings, the resulting V$_2$O$_5$–SiO$_2$ layers were subsequently nitried by ammonia treatment at the temperature 1200$^\circ$C. The nitridation was carried out in a silica glass tube under NH$_3$ gas flow (41 l/h) at a heating rate of 1$^\circ$C/min from the room temperature to 1200$^\circ$C and then held isothermally at this temperature for 1 h. After that the samples were cooled under NH$_3$ gas flux. To examine the influence of the film thickness on superconducting properties, the $x = 80$ samples with the thickness 300, 750 and 1050 nm were prepared. In this case the preparation procedure before nitridation process was repeated respectively two, five and seven times. The thickness of the samples was determined using profilometer.

Measurements of resistivity as a function of temperature were performed in the temperature range of 5–300 K, with a DC technique in the standard four — terminal configuration. The resistivity is described as a sheet resistivity ($\Omega/\square$), because the measurements were performed on thin films.

The structure investigations of the VN–SiO$_2$ films were described in [5].
3. Results and discussion

Figure 1 illustrates the temperature dependencies of the sheet resistivity of the 450 nm thick xVN-(100-x)SiO₂ (where x = 90, 80, 70 and 60 mol%) films. All the samples apart the x = 90 one, exhibited superconducting transition. The lowest resistivity before superconducting transition was obtained for x = 70. For this sample the global superconducting transition is also seen. The critical temperatures T_{conset} of the samples x = 80, 70 and 60, were about 7.5 K. The small drop of resistivity observed for x = 90 sample at about 6.7 K may suggest, that only a few percent of VN grains became superconducting and global superconductivity is not reached in this sample. As it was shown by Roberts et al. [6], even small deviation from stoichiometry or the presence of V-O bonds in the system can change the superconducting properties of the system. Only VN crystalline phase was seen in X-ray Diffraction (XRD) measurements of the samples, but the small amount of V-O bonds was seen in X-ray Photoelectron Spectroscopy (XPS) spectra [5]. This could lead to the situation that not all grains became superconducting. It should be noticed that x = 90 sample examined with magnetically modulated microwave absorption (MMMA) also did not exhibit superconducting transition [5]. Recently it has been reported, that Si addition may improve some physical properties of NbN [7]. A similar behavior was observed in NbN-SiO₂ samples [8]. In this case SiO₂ addition improved superconducting properties of the samples. It could be possible, that SiO₂ helps in formation of Josephson junction between VN grains. If to consider this suggestion it can be that in x = 90 sample, SiO₂ content is too low to observe global superconductivity.

A convenient measure of disorder in moderate-to-strong superconductors, can be the residual resistance ratio rₐ, equal to the ratio of the resistances at 300 and 10 K [9, 10]. The rₐ of well-ordered, stoichiometric VN films can be as high as 8–9 [4, 9]. In the present work rₐ was independent of the VN-SiO₂ ratio and about 1.1. This value suggests that the VN grains form disordered system. The temperature dependence of resistivity of the samples above superconducting transition is not linear. At low temperatures (T_c < T < 0.1θ_D, where θ_D is the Debye temperature) nonmagnetic pure metals, as well as moderate and strong coupled superconductors show "classical" behavior of the temperature dependence of resistivity ρ(T) ≈ Tⁿ, where n = 3–5. When the disorder of the system increases, n decreases in a monotonous way, finally reaching n = 2, independent on the nature of disorder [9–11]. Index n calculated by Zasadzinski et al. [9] for well-ordered, stoichiometric VN films prepared by reactive DC sputtering was n = 4. In the present work the temperature dependence of resistivity satisfies the relation: ρ(T) ≈ Tⁿ, where n is between 2.4 and 2.7, which is close to the T² region. This may confirm the suggestion that VN in presented films forms disordered system. The n coefficient is independent of the VN-SiO₂ ratio. An exemplary dependence for x = 60 film is shown in Fig. 2. The results of sheet resistivity of the VN samples

![Fig. 1. Temperature dependence of sheet resistivity of xVN-(100-x)SiO₂ (where x = 90, 80, 70, 60 mol%) films.](image)

![Fig. 2. Resistivity of x = 60 sample as a function of T, where n = 2.5.](image)
4. Conclusions

It may be seen from electrical resistivity results, that ammonolysis of $V_2O_3$–SiO$_2$ sol–gel derived films could be a promising method of superconducting VN–SiO$_2$ films preparation. It may be possible, that SiO$_2$ addition can improve the superconducting properties of VN–SiO$_2$ samples, as it happens in NbN–SiO$_2$ films prepared with the same method [8], however the reason of this behavior is not clear yet. The best superconducting properties were observed for $x = 70$ sample. It may be suggested from the temperature dependence of resistivity in the low temperature region, that the VN grains form a disorder system. The critical temperatures of the samples $T_{c onset}$ are about 7.5 K, what is a little bit lower than usually observed for well-ordered, stoichiometric VN. This may be caused by lattice disorder connected with non uniform nitrogen distribution during the ammonolysis process.

References