

Transport Properties of Nitrided VN–SiO₂ Sol–Gel Derived Films

B. KOŚCIELSKA*

Faculty of Applied Physics and Mathematics, Gdańsk University of Technology

Narutowicza 11/12, 80-233 Gdańsk, Poland

This work presents transport properties of x VN–(100– x)SiO₂ (where $x = 90, 80, 70, 60$ mol%) films. The films were prepared by thermal nitridation of sol–gel derived V₂O₃–SiO₂ (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 V₂O₃–SiO₂ coatings leads to the formation of disordered structures, with VN metallic grains dispersed in the matrix of insulating SiO₂. The critical temperatures of the superconducting transition of the samples T_{conset} are about 7.5 K.

PACS: 81.20.Fw, 74.78.–w, 74.70.Ad

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 ≈ 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 V₂O₃–SiO₂ coatings, disordered structure with VN metallic grains dispersed in the matrix of insulating SiO₂ is obtained

2. Experimental

The films with a composition x VN–(100– x)SiO₂ (where $x = 90, 80, 70$ and 60 mol%) were obtained by

thermal nitridation of V₂O₃–SiO₂ sol–gel derived films (in a proper V₂O₃/SiO₂ 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 V³⁺ 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 °C for 1 hour. Repeating the above procedure three times gave approximately 450 nm thick films. To obtain VN–SiO₂ coatings, the resulting V₂O₃–SiO₂ layers were subsequently nitrided by ammonia treatment at the temperature 1200 °C. The nitridation was carried out in a silica glass tube under NH₃ gas flow (4 l/h) at a heating rate of 1 °C/minute from the room temperature to 1200 °C and then held isothermally at this temperature for 1 h. After that the samples were cooled under NH₃ 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 (Ω/\square), because the measurements were performed on thin films.

The structure investigations of the VN–SiO₂ films were described in [5].

* corresponding author; e-mail: basia@mif.pg.gda.pl

3. Results and discussion

Figure 1 illustrates the temperature dependencies of the sheet resistivity of the 450 nm thick x VN-(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 (MMA) 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.

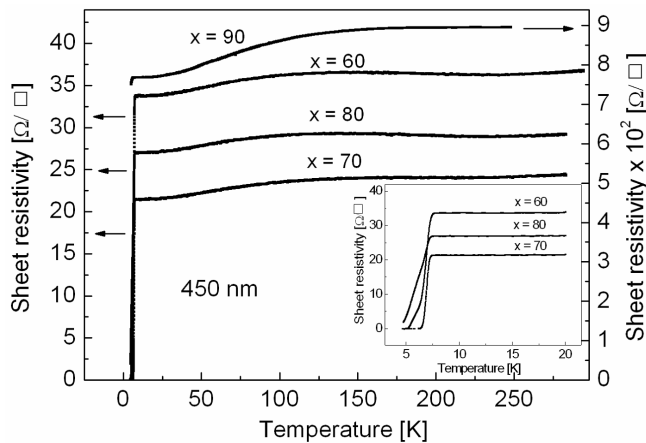


Fig. 1. Temperature dependence of sheet resistivity of x VN-(100- x)SiO₂ (where $x = 90, 80, 70, 60$ mol%) films.

A convenient measure of disorder in moderate-to-strong superconductors, can be the residual resistance ratio r_R , equal to the ratio of the resistances at 300 and 10 K [9, 10]. The r_R of well-ordered, stoichiometric VN

films can be as high as 8–9 [4, 9]. In the present work r_R 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 ($T_c < T < 0.1\theta_D$, 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 $\rho(T) \propto T^n$, 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: $\rho(T) \propto T^n$, where n is between 2.4 and 2.7, which is close to the T^2 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

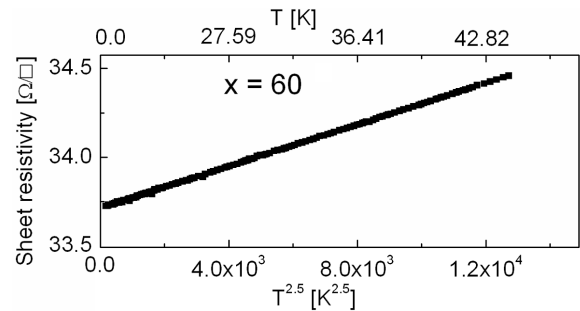


Fig. 2. Resistivity of $x = 60$ sample as a function of T^n , where $n = 2.5$. The index n for all the samples was calculated by the least square method. To obtain the best fitting, n was changed in step of 0.1 in the range from 1 to 4 and for each n value standard deviation was calculated. The minimum of standard deviation in the function of n corresponds the proper n value.

($x = 80$) of the thickness of 300, 450, 750 and 1050 nm are shown in Fig. 3. All the samples exhibit superconducting transition. The critical temperatures T_{conset} of the samples increases slightly with the thickness increase, from 7.5 to 8.2 K. As it was discussed in the literature [12–14], the electrical conductivity and superconducting properties of thin films strongly depend on their thickness. Although this phenomenon occurs mainly in ultra-thin systems. In the present work this phenomenon may be connected with the way of sample preparation. It is possible that better microporous system, before the nitridation process, is created in thicker samples. The microporous structure allows both a significant incorporation of nitrogen and its distribution through the film. This could lead to the increase of T_{conset} with the film thickness increasing. All these samples in the temperature region $T_c < T < 0.1\theta_D$ obey the relation: $\rho(T) \propto T^n$,



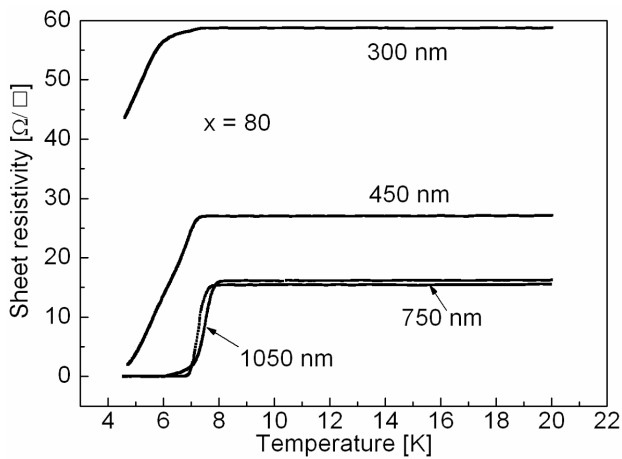


Fig. 3. The temperature dependence of sheet resistivity of $x = 80$ films with increasing thickness.

where n is between 2.4 and 3. The thickness of the sample does not influence the value of n .

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_{conset} 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 not uniform nitrogen distribution during the ammonolysis process.

References

- [1] S.T. Oyama, *Catal. Today* **15**, 1 (1992).
- [2] H. Kwon, S. Choi, L.T. Thompson, *J. Catal.* **184**, 236 (1999).
- [3] B.R. Zhao, L. Chen, H.L. Luo, M.D. Jack, D.P. Mullin, *Phys. Rev. B* **29**, 6198 (1984).
- [4] K.E. Gray, R.T. Kampwirth, D.W. Capone II, R. Vaglio, J. Zasadzinski, *Phys. Rev. B* **38**, 2333 (1988).
- [5] B. Kościelska, A. Winiarski, W. Jurga, *J. Non-Cryst. Solids* **356**, 1998 (2010).
- [6] B.W. Roberts, *J. Phys. Chem. Ref. Data* **5**, 581 (1976).
- [7] J. Wang, Z. Song, K. Xu, *Surf. Coat. Technol.* **201**, 4931 (2007).
- [8] B. Kościelska, W. Jurga, *J. Non-Cryst. Solids* **354**, 4345 (2008).
- [9] J.F. Zasadzinski, A. Saggese, K.E. Gray, R.T. Kampwirth, R. Vaglio, *Phys. Rev. B* **38**, 5065 (1988).
- [10] J. Zasadzinski, R. Vaglio, G. Rubino, K.E. Gray, M. Russo, *Phys. Rev. B* **3**, 2929 (1985).
- [11] M. Gurvitch, *Phys. Rev. Lett.* **56**, 647 (1986).
- [12] Y. Imry, M. Strongin, *Phys. Rev. B* **24**, 6353 (1981).
- [13] H.M. Jaeger, D.B. Haviland, A.M. Goldman, B.G. Orr, *Phys. Rev. B* **34**, 4920 (1986).
- [14] R.P. Barber, Jr., R.C. Dynes, *Phys. Rev. B* **48**, 10618 (1993).