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Influence of sputtering parameters on the main characteristics of ultra-thin vanadium nitride films

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Influence of sputtering parameters on the main characteristics of ultra-thin vanadium nitride films

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Abstract. We researched the relation between deposition and ultra-thin VN films parameters. To conduct the experimental study we varied substrate temperature, Ar and N_2 partial pressures and deposition rate. The study allowed us to obtain the films with close to the bulk values transition temperatures and implement such samples in order to fabricate superconducting single-photon detectors.

1. Introduction

Over the last years dramatic influx of interest was received by the field of superconducting devices. They already found its place in many important research areas such as radio astronomy and quantum processing experiments [1, 2]. In all of these devices the key role is given to a thin (<100 nm) superconducting films which are fabricated in different incarnations. Main parameters of the films such as superconductor energy gap (Δ), resistivity (ρ) and thickness (d) form a device specifications and by that its implementation area. Many decades niobium nitride (NbN) was the material of choice for such applications because of its relatively high transition temperature (T_c), which has been demonstrated on a wide range of substrate materials and deposition techniques. This material happens to have a wide range of each parameter [3]. Although it was discovered recently that only specific range of the NbN film parameters leads to the high performance of superconducting devices, in particular – superconducting single-photon detectors (SSPD) [4]. It was also found that the characterization of the NbN superconducting properties could be sophisticated due to the presence of few upper and under layers of the film [5], and because of that, most of the material properties calculations, which are thickness-dependent, are either unreliable or complex to perform. To test the versatility of these recent discoveries, we researched a new material – vanadium nitride. The material shows no strong correlation between the deposition and superconducting parameters, and has a relatively high T_c with respect to popular amorphous material such as WSi [6, 7]. In this work we show that VN has a potential as SSPD material as well as its peculiar properties which need further understanding.

2. Production and experimental study

The properties of superconducting vanadium nitride films were studied earlier [6, 8]. Although, this material has never been used for superconducting devices fabrication, such as hot-electron bolometers (HEB) and SSPDs, before our investigation. Therefore, there is no information related to research of ultra-thin VN films and its features. Our study was focused on the films with thicknesses <15 nm, which we used for SSPD fabrication [9]. And the films 15-40 nm thick were used to define main characteristics of the films avoiding its suppression by the thickness [10].

As well as many other materials, we deposited our films using reactive magnetron sputtering. Deposition was performed in AJA International Inc. Orion series system using vanadium (99.9 %) 2” target that was sputtered in Ar and N_2 atmosphere. The deposition was performed onto commonly-used Si, Si/SiO_2 and Si/Si_3N_4 substrates with the typical background pressure of $<8\cdot10^{-8}$ Torr. In order to study the dependencies of the main thin films characteristics on deposition parameters we changed total pressure (P_{tot}), N_2 concentration, substrate temperature (T_{sub}) and deposition rate (by discharge current). These parameters are considered to influence the stoichiometry of the films and are precisely controlled in case of NbN deposition in order to obtain films with desired parameters [3, 11]. Besides standard for thin and ultra-thin films sheet resistance (R_s) dependency of T_c, new tendencies, which are related to study of the disordered films, also require obtaining the T_c dependency on residual resistivity ratio ($RRR=R_{300K}/R_{20K}$) and ρ ($\rho = R_s/d$) [4, 12]. These dependencies for the VN ultra-thin films are presented on figure 1. To obtain this data, the variation of P_{tot} (in the range 0.5 – 9 mTorr), T_{sub} (400-800°C) and N_2 concentration (11-28 %) in the gas mixture was performed, as well as the variation of the deposition time of the films. As it follows from the graphs, these changes did not have strong influence on the films parameters. However, we should note that the highest values of T_c were obtained at higher deposition rates (higher discharge currents) of ~3 nm/min. Obtained maximal T_c of 8.3 K for ~34 nm thick film is very similar to the one obtained with ≥0.5 µm films in works [6, 8]. The major difference of the VN films RRR with respect to the NbN films with thicknesses of <10 nm could be noticed on figure 1b. Even for the films with suppressed values of the transition temperature, the RRR remained above 1.

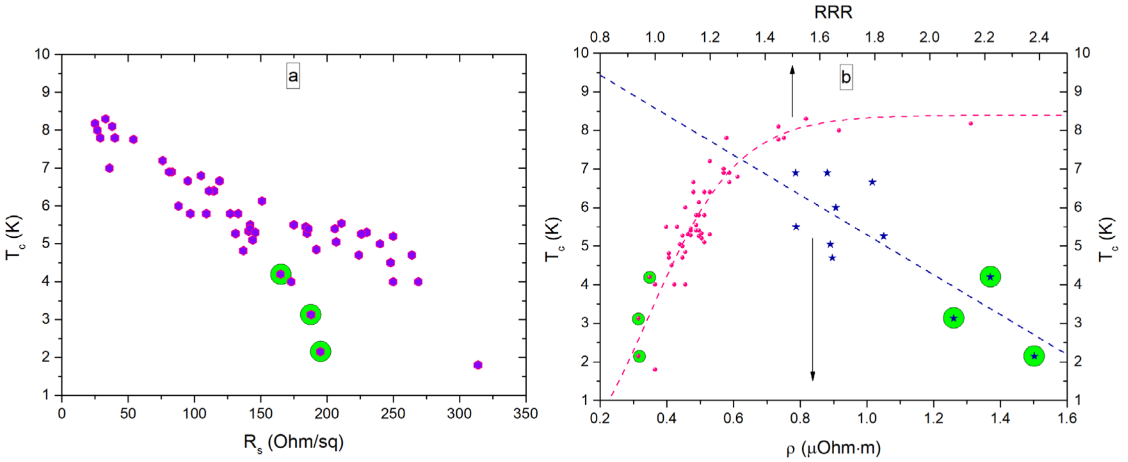

Figure 1. Transition temperature dependencies on the main VN films parameters: **(a)** sheet resistance; **(b)** resistivity and residual resistivity ratio. Green circles highlight the films, which were deposited in pure N_2 atmosphere

To research the extreme way of changing the films characteristics, we excluded the Ar from the gas mixture and performed the series of films depositions in N_2 atmosphere. This experiment resulted in films (highlighted on fig 1 by the green circles) that differ from the majority of the data points by its parameters. In overall these tests showed that thin VN films have only slight change of its parameters even when the deposition process is drastically changed. We believe that such behavior could be related to the formation of the single-phase material among all of the deposition parameters. This contrasts with the well-known phase mixture that exists in thin NbN films deposited with non-optimal parameters or substrates which do not ensure agreement between the lattices [11]. This result could benefit to the VN films over other polycrystalline materials such as NbN (NbTiN), TaN and TiN.

As it was pointed out in many works, in case of ultra-thin superconducting films there are upper and under layers of the superconducting stratum [4, 5]. Our results on the resistivity measurements were realized with the data obtained by X-ray Photoelectron Spectroscopy (XPS), which allows the definition of depth profile of the films [5, 13] (excluding the cases when the film thickness is more than 13 nm). The novelty and reliability of the method bring major refinements in the main superconducting parameters calculations and therefore is well appreciated, especially in case of the new thin-film materials. In our experiments it allowed to utilize the thickness data more precise than the standard AFM-based measurements. For example, in 6 nm deposited film only 2.4-3 nanometers remained supposedly superconductive (see Table 1) and therefore only this thickness should be considered in ρ calculations.

XPS study of the films was performed with the help of the electron-ion spectroscopy module based on Nanofab 25 (NT-MDT) platform. In the analysis chamber was an ultrahigh oil-free vacuum about 0.75 nTorr. All spectra were recorded with use of Mg anode of the X-ray source without a monochromator. The spectra were recorded with an electrostatic hemispherical energy analyzer SPECS Phoibos 225. All survey spectra scans were recorded at a pass energy of 80 eV. The detailed scans of distinctive lines were in most cases recorded as wide as needed just to encompass the peak(s) of interest and were obtained with a pass energy of 20 eV.

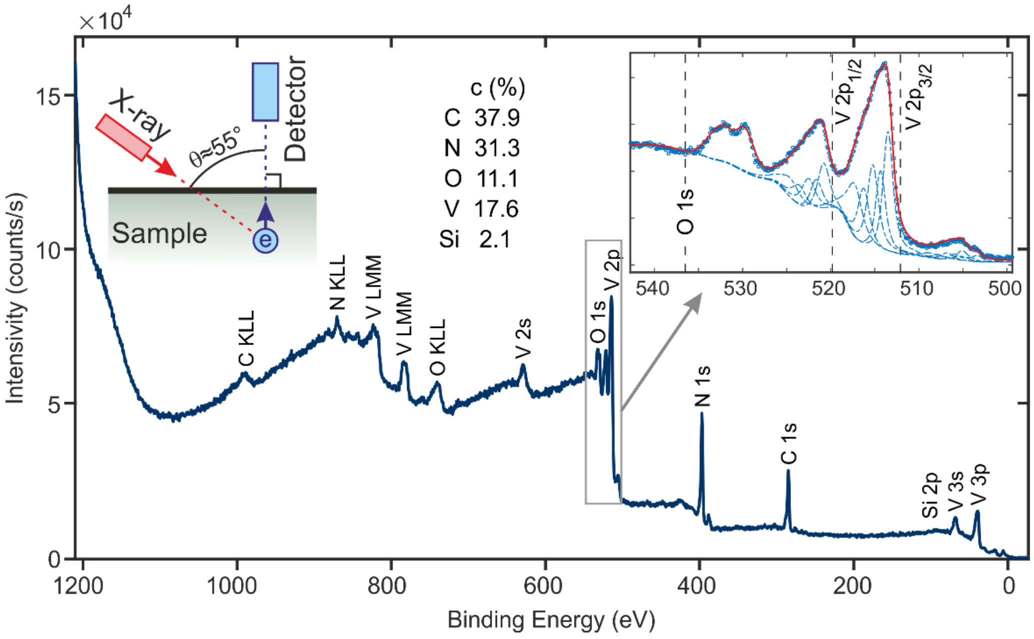

Figure 2. XPS survey spectrum of a VN film. Enlarged image in the upper right corner: decomposition of lines into partial peaks; image in the upper left corner: principle scheme of the experiment; in the upper middle relative atomic concentrations are presented.

Non-destructive chemical and phase depth profiling of the nano-scaled films in this investigation was carried out on the base of method [13], that includes a new approaches for background subtraction of multiple inelastically scattered photoelectrons considering depth inhomogeneity of electron inelastic scattering; a new method of photoelectron line decomposition into component peaks considering physical nature of different decomposition parameters; joint solution of the background subtraction and photoelectron line decomposition problems; control of line decomposition accuracy with the help of a suggested performance criterion; calculation of layer thicknesses for a multilayer target using a simple formula. In total, this method enables to determine depth profiles with sub-monolayer accuracy using XPS data.

Figure 2 displays experimental XPS data as calculated using the mentioned method. The line N1s is decomposed into three peaks corresponding to different phases of vanadium nitride: VN, VN_x and VNO_x (not shown). The line Si2p is decomposed into three peaks: Si, SiO_2 and VN_y-SiO_x (not shown).

Table 1 shows computed results for the thicknesses following the formula from work [13], which accounts for partial intensities obtained by decomposition of the lines N1s, C1s and V2p.

Table 1. Chemical and phase depth profiling of a VN film on Si substrate.

	d, nm	Formula
Σ (deposited)	**6.04**	
8	*0.58*	*hydrocarbons*
7	**0.75**	$\mathbf{V_2O_5}$
6	**0.42**	$\mathbf{VO_2}$
5	**0.6**	$\mathbf{VNO}_x$
4	**0.56**	$\mathbf{VN}_x$
3	**2.45**	**VN**
2	**1.26**	$\mathbf{VN}_y\text{-}\mathbf{SiO}_x$
1	*2.67*	SiO_2
Substrate (0)	*Inf*	*Si*

The data above shows that there is an interface between the vanadium nitride layer (#3) and the substrate (#0, #1), as between the vanadium nitride and the oxide layers (#6, #7). These transition layers contain different phases (layers #2, #4, #5). Such result is obtained for the first time.

In order to study the possibility of obtained VN films implementation in superconducting nanoelectronics, we fabricated SSPDs out of the films with different T_c and R_s. We used the same fabrication route as for our NbN SSPDs [4, 14] with one slight modification – instead of PMMA A3 electron-beam resist we used ZEP 520 A7 because of its higher resistance to plasma-chemical etching process in SF_6, which proved to be less selective to VN with respect to the NbN films. The geometries of the devices varied in nanostripe width and length. The widths were 100-130 nm, and the active area was located on 3x3, 7x7, 11x11 or 15x15 μm^2 areas with fill factor ~0.6.

Device characterization consisted of critical current (I_c) measurements of the batches that showed single-photon response, from which we then calculated critical current density (J_c). With respect to the XPS data, the average value of J_c was $\sim 1 \cdot 10^{10}$ A/m^2. This value was uncharacteristically increasing along with the nanostripe length. This phenomenon was explained by the latching problem of the SSPD, that was observed on NbN detectors before [15]. The latching disappeared at certain kinetic inductance (L_{kin}) of the nanostripe of ~ 1.5 μH, which was extracted from detector pulse shape using oscilloscope (figure 3a). To make further analysis of the VN specific kinetic inductance we studied the dependency of L_{kin} on the detectors normal-state resistance, which showed its universality in work [16]. It appeared that in average, VN devices have 2.3 times larger kinetic inductance with respect to NbN-based devices – figure 2b). Perhaps this fact could be related to the difference in the magnetic field penetration depth of these materials. Indeed, this parameter could decrease the maximal counting rates of the SSPD [15], but in contrast could benefit in superconducting imagers that were presented recently [17].

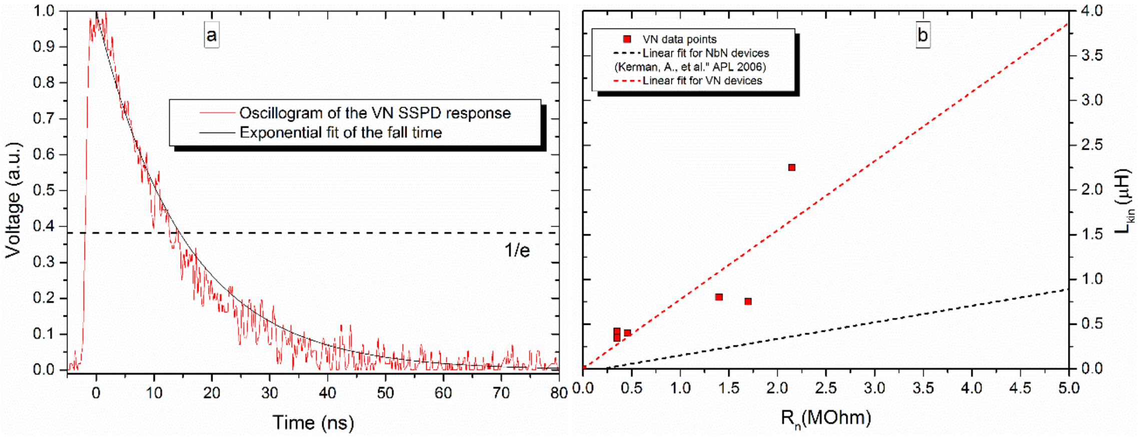

Figure 3. (**a**) The single-photon response of VN SSPD and its exponential decay. Dotted line marks the amplitude decrease down to 1/e. (**b**) SSPD resistance dependency of kinetic inductance. The kinetic inductance for VN devices was calculated indirectly with the method presented in work [16] and was mapped with the linear fit of the data for NbN devices from the same work. Each VN data point corresponds to the approximated value within the batch (~15 devices with the same geometry).

3. Conclusion

We have demonstrated main superconducting vanadium nitride films (<50 nm) parameters. The T_c dependencies on the main characteristics of the films, such as R_s, ρ and RRR were obtained. Our investigation showed that characteristics of VN films remain stable along with the variation of most of the sputtering parameters. In addition to that we applied novel method of films thickness and compound characterization. Obtained VN films were implemented in superconducting single-photon detectors and its peculiar properties were discovered.

Acknowledgments

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References

[1] Huebers, H.W., Semenov, A., Schubert, J., Gol'tsman, G.N., Voronov, B.M., Gershenzon, E.M., Krabbe, A. and Roeser, H.P., 2000, June. NbN hot-electron bolometer as THz mixer for SOFIA. In Airborne Telescope Systems (Vol. 4014, pp. 195-203). International Society for Optics and Photonics.

[2] Hadfield, R.H., 2009. Single-photon detectors for optical quantum information applications. Nature photonics, 3(12), p.696.

[3] Chockalingam, S.P., Chand, M., Jesudasan, J., Tripathi, V. and Raychaudhuri, P., 2008. Superconducting properties and Hall effect of epitaxial NbN thin films. Physical Review B, 77(21), p.214503.

[4] Smirnov, K., Divochiy, A., Vakhtomin, Y., Morozov, P., Zolotov, P., Antipov, A. and Seleznev, V., 2018. NbN single-photon detectors with saturated dependence of quantum efficiency. Superconductor Science and Technology, 31(3), p.035011.

[5] Lubenchenko, A.V., Batrakov, A.A., Krause, S., Pavolotsky, A.B., Shurkaeva, I.V., Ivanov, D.A. and Lubenchenko, O.I., 2017, November. XPS Depth Profiling of Air-Oxidized Nanofilms of NbN on GaN Buffer-Layers. In Journal of Physics: Conference Series (Vol. 917, No. 9, p. 092001). IOP Publishing.

[6] Gray, K.E., Kampwirth, R.T., DW Capone, I.I., Vaglio, R. and Zasadzinski, J., 1988. Superconducting properties of VN x sputtered films including spin fluctuations and radiation damage of stoichiometric VN. Physical Review B, 38(4), p.2333.

[7] Seleznev, V.A., Divochiy, A.V., Vakhtomin, Y.B., Morozov, P.V., Zolotov, P.I., Vasil'ev, D.D., Moiseev, K.M., Malevannaya, E.I. and Smirnov, K.V., 2016, August. Superconducting detector of IR single-photons based on thin WSi films. In Journal of Physics: Conference Series (Vol. 737, No. 1, p. 012032). IOP Publishing.

[8] Zasadzinski, J., Vaglio, R., Rubino, G., Gray, K.E. and Russo, M., 1985. Properties of superconducting vanadium nitride sputtered films. Physical Review B, 32(5), p.2929.

[9] Zolotov, P., Divochiy, A., Vakhtomin, Y., Seleznev, V., Morozov, P. and Smirnov, K., 2018. Superconducting Single-photon Detectors Made of Ultra-thin VN Films. KnE Energy & Physics, 3(3), pp.83-89.

[10] Kang, L., Jin, B.B., Liu, X.Y., Jia, X.Q., Chen, J., Ji, Z.M., Xu, W.W., Wu, P.H., Mi, S.B., Pimenov, A. and Wu, Y.J., 2011. Suppression of superconductivity in epitaxial NbN ultrathin films. Journal of Applied Physics, 109(3), p.033908.

[11] Marsili, F., 2009. Single-photon and photon-number-resolving detectors based on superconducting nanowires.

[12] Burdastyh, M.V., Postolova, S.V., Baturina, T.I., Proslier, T., Vinokur, V.M. and Mironov, A.Y., 2017. Superconductor–Insulator Transition in NbTiN Films. JETP Letters, 106(11), pp.749-753.

[13] Lubenchenko A. V. et al. 2017 Applied Surface Science. 427. 711–721.

[14] Zolotov, P.I., Divochiy, A.V., Vakhtomin, Y.B., Morozov, P.V., Seleznev, V.A. and Smirnov, K.V., 2017, November. Development of high-effective superconducting single-photon detectors aimed for mid-IR spectrum range. In Journal of Physics: Conference Series (Vol. 917, No. 6, p. 062037). IOP Publishing.

[15] Yang, J.K., Kerman, A.J., Dauler, E.A., Anant, V., Rosfjord, K.M. and Berggren, K.K., 2007. Modeling the electrical and thermal response of superconducting nanowire single-photon detectors. IEEE transactions on applied superconductivity, 17(2), pp.581-585.

[16] Kerman, A.J., Dauler, E.A., Keicher, W.E., Yang, J.K., Berggren, K.K., Gol'Tsman, G. and Voronov, B., 2006. Kinetic-inductance-limited reset time of superconducting nanowire photon counters. Applied physics letters, 88(11), p.111116.

[17] Zhao, Q.Y., Zhu, D., Calandri, N., Dane, A.E., McCaughan, A.N., Bellei, F., Wang, H.Z., Santavicca, D.F. and Berggren, K.K., 2017. Single-photon imager based on a superconducting nanowire delay line. Nature Photonics, 11(4), p.247.