Superconductivity of Niobium Thin Films
in the BiOCl/Nb Heterostructures

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In the current paper, electrical transport properties of 25 nm thick Nb films sputtered on the photosensitive semiconductor BiOCl were investigated in the temperature range $7.5 \text{ K} \leq T \leq 8.5 \text{ K}$. The influence of green (532 nm) and red (640 nm) laser excitations on resistive superconducting transitions of the niobium thin films on a silicon glass and BiOCl single crystal substrates were studied. The temperature dependences of the resistivity for Nb in BiOCl/Nb are in good agreement with the McMillan model which indicates the strong influence of the inverse proximity effect induced by the interface. The increased influence of the BiOCl/Nb interface under laser excitation corresponds to the raising of the ratio of the density of normal to superconductivity carriers in the $T \to 0$ limit and this observation is in agreement with the photoconductivity study of BiOCl single crystals.

DOI: 10.12693/APhysPolA.131.1030
PACS/topics: 74.25.F–, 68.35.bg, 74.45.+c

1. Introduction

In the past decade, attention was paid to the light-induced effect in superconductors [1–3]. Under laser excitation, it is possible to manipulate the surface density of state, to change superconducting properties. Another possibility to change the local density of states arises from proximity induced effects [4]. One can manipulate the superconducting density of states at the interface using photosensitive semiconductor/superconductor heterostructures. Bismuth oxyhalides BiOX ($X = \text{F, Cl, Br and I}$) photosensitive semiconductors that have attracted intensive attention due to their characteristic photoelectric properties and possible technological applications [5, 6]. Due to their layered structure and facile fabrication by exfoliation [7], single crystals with thicknesses less than 1 $\mu\text{m}$ could be used as a substrate for semiconductor/superconductor heterostructures.

The electrical transport properties of thin Nb films, with nominal thicknesses of 25 nm, supported on Si glass or BiOCl single crystal substrates were investigated in the temperature range $7.5 \text{ K} \leq T \leq 8.5 \text{ K}$ with and without laser excitation. The temperature dependences of resistivity for Nb on Si glass overlapping with each other indicating an excellent stability of interface. The resistive curves at the vicinity of superconducting transition for Nb on BiOCl single crystal are in good agreement with the McMillan model [8], which indicates the strong influence of the inverse proximity effect induced by the interface. The calculated depth of the interface is approximately 0.85 nm. The increased influence of the interface under the laser excitation corresponds to the raising in $N_N(0)/N_S(0)$ ratio ($N_N,S(0)$ are the density of states in normal (N) and superconducting (S) layers at $T = 0$). It is in agreement with the photoconductivity spectra of BiOCl single crystals obtained in [9].

2. Experimental details

In this work, a magnetron sputtering technique was used to generate Nb films with nominal thicknesses of 25 nm. Sputtering conditions were: chamber pressure $3.7 \times 10^{-10} \text{ Pa}$, argon pressure $3 \times 10^{-5} \text{ Pa}$, DC target power 270 W, substrate temperature 22$\text{°C}$. The thickness of the sputtered films was controlled by quartz crystal microbalance device. The films were simultaneously deposited on commercially purchased Si glass slides 20 mm $\times$ 20 mm $\times$ 0.5 mm and BiOCl single crystal 10 mm $\times$ 5 mm $\times$ 1 $\mu\text{m}$ obtained by exfoliation method [7]. The high-quality BiOCl single crystal that served as the source of the thin films was synthesized using gas transfer methods briefly described in [9].

Fig. 1. Schematic representation of electric transport measurements. (a) 25 nm Nb sputtered on the Si glass and (b) 25 nm Nb sputtered on the BiOCl.

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The electrical resistivity of the Nb thin films was obtained by the four-point probe measurements of a direct current using Keithley 6221 current source and Keithley 2182A nanovoltmeter. Temperature control was performed using the commercial Physical Property Measurement System (PPMS). Temperature dependences were obtained in both cooling and heating modes at two temperature rates 0.1 K/min and 0.3 K/min. Thermal contact was established by installing sample on a massive Cu plate glued with the GE-Varnish (see scheme in Fig. 1). Electric contacts were made using the silver conducting paste with annealing at 80°C during 10 min. The thin sapphire plate was used to avoid short circuit or current leaking. Laser excitation with the power 15 mW/cm² was applied on either Nb (Fig. 1a) or the photosensitive semiconductor BiOCl (Fig. 1b). Laser excitations with 532 nm (2.33 eV) and 640 nm (1.94 eV) were obtained by two CNI laser devices with the maximum power 300 mW and 200 mW, respectively. Output laser power was measured using thermal power sensor (Ophir, 3A-P). Resistive curves were measured at the current 1 µA.

3. Results and discussion

The experimental results of the superconducting transition for the Nb films under various mounting and irradiation conditions are given in Fig. 2. It is noteworthy that the data for the transitions were acquired with warming and cooling protocols at two different rates, and the results for a specific mounting/irradiation conditions were independent of the various measuring conditions. This observation indicates that a high-quality thermal contact exists between the sample and the cold plate of the PPMS, and consequently, the laser excitation does not significantly perturb the temperature of the sample. Only the curves measured at temperature rate 0.1 K/min in cooling mode are plotted in Fig. 2.

![Fig. 2. Temperature dependences of normalized resistivity of 25 nm Nb thin films on Si glass (circles); on BiOCl without laser excitation (black squares), under green (green squares) and red (red squares) laser excitation.](image)

Critical temperatures were identified by the maximum value of \(dp/dT\) curves (Fig. 3), and the results are tabulated in Table I. The width of superconducting transitions was identified in the temperature range from deviation from normal state behavior till the state \(\rho \to 0\) (Fig. 2). The thin film sputtered on Si glass has a critical temperature 8.2 K along with the width of superconducting transition \(\Delta T_c \approx 0.2\) K and the residual resistance ratio (RRR) \(\approx 4.3\) indicates a high quality of the thin film. All measured curves, both without and with laser excitation, perfectly match each other, and this result is a consequence of an interface with excellent stability.

![Fig. 3. Temperature dependences of \(dp/dT\) for 25 nm Nb thin films on Si glass (circles); on BiOCl without laser excitation (black squares), under green (green squares) and red (red squares) laser excitation.](image)

<table>
<thead>
<tr>
<th>Conditions</th>
<th>(T_c) [K]</th>
<th>(\Delta T_c) [K]</th>
</tr>
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<tbody>
<tr>
<td>Si glass without laser</td>
<td>8.22</td>
<td>8.17</td>
</tr>
<tr>
<td>red light</td>
<td>8.22</td>
<td>8.15</td>
</tr>
<tr>
<td>green light</td>
<td>8.22</td>
<td>8.02</td>
</tr>
</tbody>
</table>

TABLE I

The superconducting transitions of Nb on the BiOCl substrate shift to the lower temperatures with increase of the laser excitation energy. The residual resistance ratio measured without laser excitation 3.8, which is slightly lower compared to the Si glass substrate. The higher width of the superconducting transition \(\Delta T_c\) and the presence of the second, low-temperature peak \(\rho / dT\) curves could indicate the phase separation in Nb thin films. With and without irradiation, the RRR for Nb on BiOCl is the same, so the defect concentration is constant during all measurements. On the other hand, the width of the superconducting transition \(\Delta T_c\) usually indicates the impureness of the sample and this parameter increased sufficiently under laser excitation.
Such a behavior could be explained regarding inverse proximity effect [10]. Despite the good quality of thin films, which indicates in RRR \( \approx 4 \), the pure Nb single crystals have RRR up to 2600 [11]. Consequently, the approximation in dirty limit could be used. According to Ashcroft [12], the electron mean free path was estimated as \( l = (\rho_\mu/\rho_\mu S)^2 \times 92 \, \text{Å} \), where \( \rho_\mu \) is a sheet resistance in \( \mu \Omega \, \text{cm} \) and ratio \( r_s/a_0 \) for Nb equals 3.07. The experimental value of sheet resistance is \( \rho_\mu = 3.09 \, \mu \Omega \, \text{cm} \), which leads to the \( l \approx 28 \, \text{nm} \). Since the sample thickness \( d \) is less than the electron mean free path \( l \), the former was used to evaluate the coherence length in the dirty limit [12] as \( \xi = 0.852 \sqrt{\text{cm} \rho_\mu} \). Assuming \( \xi_0 = 38 \, \text{nm} \) for bulk Nb [10], then this analysis yields \( \xi = 26 \, \text{nm} \). This value is very close to the thickness of our Nb film \( d = 25 \, \text{nm} \) and places our study in the two-dimensional limit. According to the McMillan model [8], the inverse proximity effect in a planar thin film geometry is an appropriate description of our experimental conditions. Consequently, the critical temperature \( T_c \) is suppressed by the normal state interface with the thickness \( d_N \) described by the equation

\[
T_c = T_{c0} \left( \frac{3.56 T_D}{T_{c0} \pi} \right)^{-\alpha/d}, \tag{1}
\]

where \( T_D = 277 \, \text{K} \) is the Nb Debye temperature, \( T_{c0} = 9.22 \, \text{K} \) is the Nb bulk critical temperature [10] and \( \alpha = d_N N_N(0)/N_S(0) \). Considering a \( N_N(0)/N_S(0) \) equals to one without laser excitation, the calculated value of \( d_N \) was estimated as 0.85 nm. Under the laser excitation, the only parameter in Eq. (1) being changed is \( \alpha \). Consequently, increase of the \( N_N(0)/N_S(0) \) ratio leads to the suppression of the superconductivity. Changes for \( N_N(0)/N_S(0) \) ratio are 1.02 under the red light excitation and 1.15 under the green light excitation. Such behavior is in good agreement with photoconductivity spectra obtained in [9] for BiOCl single crystals.

4. Conclusions

The electrical transport properties of 25 nm Nb thin films were investigated in a temperature range 7.5 K \( \leq T \leq 8.5 \, \text{K} \) on Si glass and BiOCl substrates with and without laser excitation. Resistive curves with and without laser excitation for Nb on Si glass matched with each other which indicates a good stability of interface and parameters in Eq. (1). The temperature dependences of resistivity of Nb on BiOCl single crystal are in good agreement with the McMillan model which indicates the strong influence of inverse proximity effect induced by the interface. The calculated depth of the normal state interface is \( d_N \approx 0.85 \, \text{nm} \). The increased influence of the interface under the laser excitation corresponds to the enlarging in \( N_N(0)/N_S(0) \) ratio which is in agreement with the photoconductivity study of BiOCl single crystals.

Acknowledgments

This work was supported by the ERDF EU (European Union European regional development fund) grant, under the contract No. ITMS 26220120005, ITMS 26220220186, APVV 0605-14 and VEGA 1-0409-15. We thank Professor M.W. Meisel for the fruitful discussions and comments that improved the manuscript.

References