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Phys. Status Solidi B, 1–4 (2016) / DOI 10.1002/pssb.201600235

physica status solidi b
www.pss-b.com
basic solid state physics

Selenium capped monolayer $NbSe_2$ for two-dimensional superconductivity studies

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Received 15 April 2016, revised 14 July 2016, accepted 18 July 2016
Published online 8 August 2016

Keywords monolayer niobium diselenide, superconductivity, molecular beam epitaxy, *in situ*

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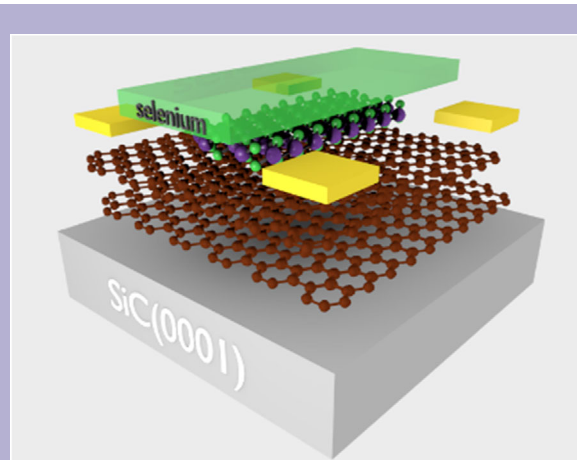
Superconductivity in monolayer niobium diselenide ($NbSe_2$) on bilayer graphene is studied by electrical transport. Monolayer $NbSe_2$ is grown on bilayer graphene by molecular beam epitaxy and capped with a selenium film to avoid degradation in air. The selenium capped samples have $T_C = 1.9\,K$. *In situ* measurements down to 4 K in ultrahigh vacuum show that the effect of the selenium layer on the transport is negligible. The superconducting transition and upper critical fields in air exposed and selenium capped samples are compared.



Schematic of monolayer $NbSe_2$/bilayer graphene with selenium capping layer and electrical contacts.

1 Introduction Interest in the layered compound, niobium diselenide ($NbSe_2$), has reemerged since the isolation of graphene from graphite [1]. $NbSe_2$ is abundant in phase transitions with a charge density wave state below 33 K and superconductivity below 7.2 K [2]. An early study on $NbSe_2$ down to bilayers has observed a decrease in the critical temperature (T_C) of superconductivity as the layer number is reduced and predicted the monolayer T_C to be 3.8 K from extrapolation [3]. Recently, both the charge density wave and the superconductivity in monolayer $NbSe_2$

have been investigated [4–7]. Although, there are discrepancies among observed monolayer T_C, they all fall below the extrapolated value of 3.8 K. Remarkably, the upper critical field of monolayer $NbSe_2$ has been found to greatly exceed the Pauli paramagnetic limit for the field parallel to the layer [6].

In most studies on ultrathin $NbSe_2$, samples were prepared by mechanical exfoliation from bulk and capped with hexagonal boron nitride or graphene [4, 6–8]. Encapsulation of monolayer $NbSe_2$ is necessary because thin $NbSe_2$ has been known to degrade in air, possibly due to photo-oxidation [9]. In an alternate system, monolayer $NbSe_2$ has been grown by molecular beam epitaxy (MBE) on bilayer graphene and capped with a $\sim$10 nm thick film of selenium [5]. The MBE prepared samples have a complimentary feature in that the selenium cap can be evaporated off to re-expose the surface. Surface sensitive techniques, such as scanning tunneling microscopy (STM) and photoemission have benefitted from the ability to expose the surface prior to an *in situ* study [5]. Especially for STM, the bilayer graphene substrate has proven effective in providing a smooth, flat surface.

We characterize the superconductivity in a MBE grown $NbSe_2$ on bilayer graphene by electrical transport down to 75 mK and under magnetic fields up to 9 T in the out-of-plane and in-plane directions. *In situ* studies at ultrahigh vacuum down to 4 K show that the selenium cap does not significantly change the electronic transport in the material. In the absence of the selenium cap, brief exposure to air causes the T_C to go down and the transition to broaden. When the superconducting transitions in selenium capped and air exposed samples are normalized by their T_C, a large relative change above T_C and negligible change below T_C is observed. Furthermore, the upper critical fields (B_{C2}) perpendicular to the layer are compared. As expected, the air exposed sample has a significantly lower B_{C2}. Even after rescaling the temperature dependence of B_{C2} by the reduction in T_C, the rescaled B_{C2} behavior is still suppressed compared to the selenium capped sample.

2 Results The device shown by the schematic in the inset of Fig. 1 is prepared as previously reported [5]. Bilayer graphene is grown epitaxially on silicon carbide and monolayer $NbSe_2$ is grown by MBE on top of the bilayer graphene. A selenium capping layer is deposited *in situ* to cover the $NbSe_2$ portion. Contacts are deposited on the areas of exposed graphene and the dc resistance of the sample is measured in a four-point probe configuration. Figure 1 shows the temperature dependence of the resistance. The sharp drop in resistance indicates a superconducting transition. We define T_C as the resistive midpoint. Without magnetic field, the sample resistance starts to deviate from normal state behavior at the onset temperature $T_{onset} = 2.6$ K. The resistance reaches half of the normal state value at $T_C = 1.9$ K and flattens out to a value close to zero at $T_{zero} = 1.3$ K. The finite resistance below T_{zero} is sample dependent and values much closer to zero are observed in other samples. Previously reported T_C for thin $NbSe_2$ by Cao et al. and Xi et al. are in agreement for multi-layers down to bilayers but show discrepancy for the monolayer [6, 7]. Our results are consistent with $T_C \sim 2$ K reported by the former.

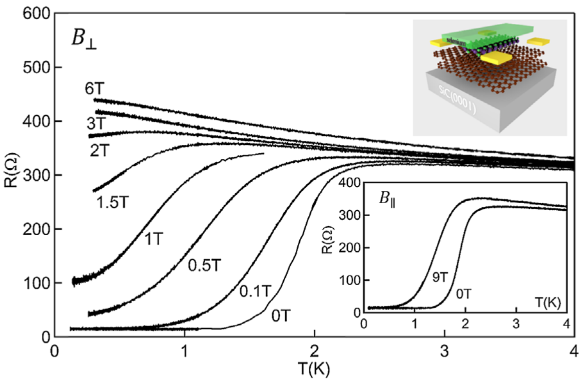


Figure 1 Resistance of selenium capped monolayer $NbSe_2$ (MBE)/bilayer graphene from 4 K to 75 mK. Each curve corresponds to the sample under a magnetic field in the direction perpendicular to the $NbSe_2$ layer ranging from 0 T to 6 T. Lower right inset: resistance of the same sample under a magnetic field in the direction parallel to the layer. The left curve corresponds to 9 T and the right curve to zero field. Top right inset: schematic of the device structure.

As expected of superconductivity, the T_C shifts to lower temperatures under a magnetic field. As shown in Fig. 1, when the magnetic field is perpendicular to the $NbSe_2$ layer, signatures of superconductivity disappear for fields above 3T. The curves for 3T and 6T show thermally activated behavior of an insulator, which is consistent with the superconductor–insulator transition for two-dimensional superconductivity [10, 11]. For the superconducting transition at $B_\perp = 1$T below T_C, the resistance starts to plateau at a larger finite value. While an intermediate metallic state in the superconductor–insulator transition has been reported for bilayer $NbSe_2$, it has not been observed in monolayer $NbSe_2$ [8]. For our system, further studies are needed to rule out other sources of finite resistance. As shown in the inset of Fig. 1, superconductivity still persists at 9T when the magnetic field is parallel to the $NbSe_2$ layer. The upper critical field is much higher than 9T for parallel fields. Although the fields are not high enough to confirm the remarkably high upper critical field in monolayer $NbSe_2$, the anisotropy is consistent with a thin film superconductor [6, 12].

To demonstrate that the selenium capping layer has negligible effect on the superconductivity in $NbSe_2$, electrical transport is compared in ultrahigh vacuum (UHV). As shown in Fig. 2, the sample is first measured with the selenium capping layer intact down to 4K. Subsequently, the selenium film is evaporated in UHV and the resistance is measured again down to 4K. The sample resistances in UHV before and after the selenium film removal have similar temperature dependences, except for an overall resistance decrease after selenium removal. It

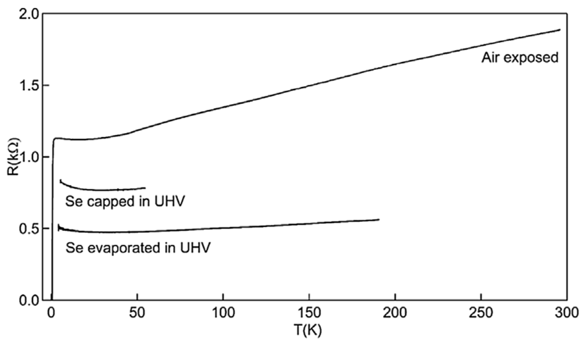


Figure 2 Comparison of monolayer $NbSe_2$ (MBE)/bilayer graphene resistance with and without selenium cap in the 4–50 K range. Lower curve corresponds to the *in situ* sample measurement in UHV after selenium cap is evaporated. Middle curve corresponds to the sample measurement in UHV prior to selenium cap evaporation. Upper curve corresponds to the sample measurement after a brief air exposure in the absence of a selenium cap.

is reasonable to expect the addition of chemical species on a monolayer to significantly change the electronics of the system. However, the interaction between the selenium film and $NbSe_2$ is possibly minimized due to the bonds between niobium and selenium being already complete in $NbSe_2$. After measurement in UHV, the sample is briefly exposed to air during a rapid transfer to a different cryostat for measurements at lower temperatures. However, the sample remains metallic and a sharp drop in resistance due to superconductivity can be seen.

As shown in Fig. 3, air exposure depresses the T_C to 0.65 K and transition broadens to span from $T_{onset} = 1.9$ K to $T_{zero} = 0.46$ K. To compare the superconducting transitions of the selenium capped and air exposed samples, the temperature for each curve is rescaled by their respective T_C values and the resistance is normalized to the resistance at T_{onset}. Above T_C, Fig. 3 shows significant broadening of the transition for the air exposed sample. The selenium capped sample reaches normal state behavior above $T/T_C = 1.4$, whereas the air exposed sample is still undergoing transition. Surprisingly, there is little difference in the transition behavior between the selenium capped sample and air exposed sample below T_C. In a superconducting transition, the portions above and below T_C are governed by two different processes [13, 14]. In cooling from the normal state to T_C, the fluctuation of the superconducting order parameter induce excess conductivity and lowers the resistance from the normal state [15]. When approaching T_C from T_{zero}, the vortex dynamics induce finite resistance from phase slip events [16]. Figure 3 shows that degradation in air impacts the fluctuation enhanced conductivity regime above T_C more heavily than the phase slippage regime below T_C. Two-dimensional superconductor behavior has been confirmed in monolayer $NbSe_2$ in both above T_C with the Aslamazov–Larkin formula and below T_C by the extraction of Berezinskii–Kosterlitz–Thouless temperature [6]. Given that a *quantum* metal state has been observed in bilayer $NbSe_2$ below T_C, it is interesting that superconductivity is preferentially protected below T_C from disorder in monolayer $NbSe_2$ [8].

Figure 4 shows the temperature dependence of the upper critical field of the selenium ($B_{C2}(T)$) capped and air exposed sample for the field perpendicular to the $NbSe_2$ layer. The selenium capped sample extrapolates to $B_{C2}(0) = 1.3$ T at zero temperature. The decrease in slope at low temperature is consistent with bulk $NbSe_2$ behavior [17]. For the air exposed sample, the upper critical field diminishes to $B_{C2}(0) = 0.2$ T. To compare both samples, $B_{C2}(T)$ is normalized by the Pauli paramagnetic limit $B_P = 1.84$ T and the temperature is divided by T_C as shown in the inset of Fig. 4 [18, 19]. Even after

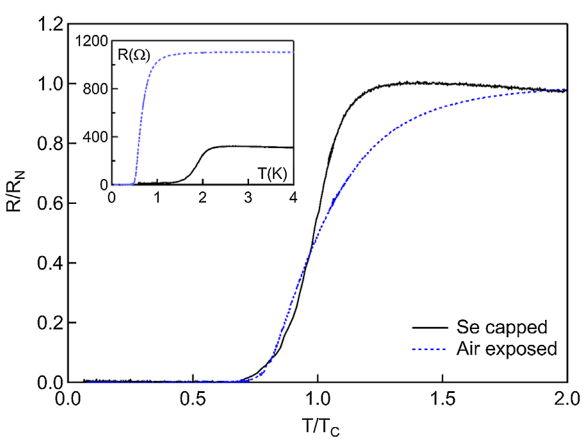


Figure 3 Rescaled superconducting transition of selenium capped and air exposed monolayer $NbSe_2$ (MBE)/bilayer graphene. For each sample, the resistance is divided by R_N, the normal state value at T_{onset}, and the temperature is divided by T_C. The solid black line corresponds to the selenium capped sample and the dotted blue line corresponds to the air exposed sample. Top left inset: the resistance measurement data prior to rescaling.

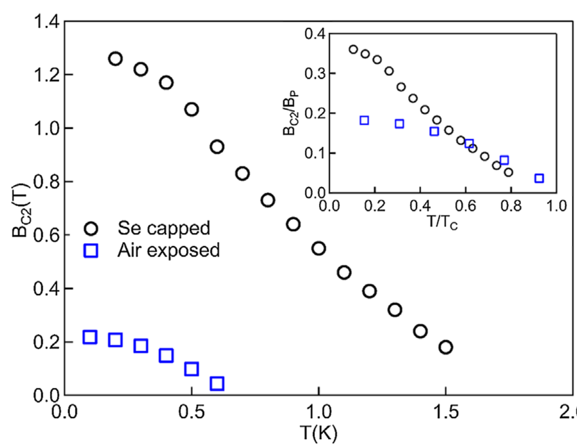


Figure 4 Upper critical field (B_{C2}) of selenium capped and air exposed monolayer $NbSe_2$ (MBE)/bilayer graphene from 75 mK to 1.5 K. Black circles correspond to the selenium capped sample and the blue squares correspond to the air exposed sample. Top right inset: the data with the B_{C2} rescaled by the Pauli paramagnetic limit $B_p = 1.84$ T and the temperature rescaled by T_C.

rescaling to account for the reduction in T_C, upper critical field behavior is more suppressed for the air exposed sample. The reduction in $B_{C2}(T)$ is more dramatic than if it were caused solely by the shift in T_C.

3 Conclusions When protected by a selenium capping layer, we find the MBE grown monolayer $NbSe_2$ on bilayer graphene is stable in air. The system displays superconducting behavior, which is consistent with earlier studies on exfoliated $NbSe_2$ and the selenium capping layer does not significantly impact the electronic transport in monolayer $NbSe_2$. Comparison of selenium capped and air exposed samples reveal that air exposure broadens the fluctuation enhanced conductivity regime above T_C. However, the T_C normalized temperature dependence of resistance in both samples remain the same in the phase slippage regime below T_C. Air exposure also suppresses the upper critical field of $NbSe_2$ by more than the effects due to the reduction of T_C.

Acknowledgements Research supported in part by the Director, Office of Energy Research, Materials Sciences and Engineering Division, of the US Department of Energy (DOE), under grant DE-AC02-05CH11231 supporting the sp2-bonded-Materials Program (magneto-transport), and by the National Science Foundation under award # DMR-1206512 (UHV transport). Synthesis was in part supported by NSF grant EFRI-2DARE 1542741. Work at the ALS is supported by DOE BES under contract no. DE-AC02-05CH11231. H.R. acknowledges support from Max Planck Korea/POSTECH Research Initiative of NRF, Korea.

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