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Electrical transport through ultrathin ordered K_3C_{60} films on Si

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Abstract

The electronic transport properties of K-doped C_{60} mono- and multi-layers are reported with focus on the superconducting transition. The films were deposited on the 7×7 reconstructed Si(111) surface in UHV and showed a well-ordered growth structure. We have measured the electrical resistivity of films with thicknesses between 1 and 6.5 monolayers (ML) in a four-probe arrangement. All films show a semiconducting temperature dependence of the resistivity even though they are doped with 3 K atoms per C_{60}. Nevertheless, we find a transition to a superconducting state for films as thin as 2.4 ML. Normal and superconducting properties are discussed in the context of disorder and film thickness.

Keywords: A. Fullerene; C. STM; D. Electronic properties, Superconductivity

1. Introduction

The electronic transport characteristics of the organic metal K_3C_{60} attracted strong experimental as well as theoretical attention after the discovery of the transition to a superconducting state at a surprising 18 K (reviews in [1,2]). The super- as well as normal-conducting properties of doped single crystals as well as amorphous films have been studied in detail. Growth and spectroscopy studies have been performed on ordered multi-layers but these systems have not been accessible for conductivity studies.

The band structure of the C_{60} crystal is based on the molecular orbitals. The LUMO-derived band is triply degenerate and can be half filled with three electrons. The structure of this phase is fcc like the undoped crystal and metallic as expected. In case of a filled band by doping with six alkalis per C_{60} the crystal structure is bcc and the system is insulating. There are five stable phases of K_xC_{60} namely $x=0$, 1, 3, 4, 6 [3]. Electronic transport measurements confirm that $x=0$, 6 are insulating, $x=1$, 4 should be metallic based on theory but just $x=1$ is, and $x=3$ was found to even superconduct with the surprisingly high $T_c=19.7$ K [4] (earlier reports were lower). The narrow band metal K_3C_{60} is quite sensitive to disorder [5] and a superconductor to insulator transition can be induced purely by removal of long range order.

Parallel to the transport studies in single crystals and amorphous films, detailed surface science knowledge has been developed about C_{60}. Growth modes of C_{60} on various single crystalline substrates have been studied as well as their density of states by spectroscopy techniques (photo emission, scanning tunneling spectroscopy). Li et al. investigated K_xC_{60} on GaAs(110) with the scanning tunneling microscope in UHV. They observed a well-ordered close packed structure already in the first layer of C_{60} and also in higher layers. The order persisted upon doping with K and the non-observability of the atoms indicates that the donor is fully ionized since the empty s-state is not accessible with the STM. Tunneling spectroscopy showed that the ordered layers of K_3C_{60} were metallic as expected from the bulk. It is important to note that well-ordered films can be doped without the introduction of disorder in contrast to amorphous films where phase separation occurs.

Recent investigations of doped ultra thin films of C_{60} have shown an anomalously high conductivity and density of states at the Fermi energy. Hebard et al. have investigated C_{60} films down to a monolayer (ML) on 4–12-nm-thick Cu films. The C_{60} is doped by charge transfer from the Cu and the overall sheet-resistance of the system drops. The resistivity of the doped film is a factor of two less than that of the alkali doped (A_3C_{60}) bulk compounds. A similar effect was observed by Tjeng et al. [6]. Their UPS

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data of a K_3C_{60} ML on Ag(111) show an increased density of states at the Fermi level compared to the bulk system.

The focus of our work is the investigation of the electronic transport properties of very thin well-ordered doped C_{60} mono- and multi-layers. The combination of epitaxially grown films on single crystal substrates together with electronic transport measurements on the length scale of growth homogeneity allows the investigation of the normal as well as superconducting properties of these interesting materials. We are approaching this regime with a contact metallization on clean reconstructed semiconducting surfaces with a probe distance between 50 and 250 nm. We have fabricated these contacts and studied the resistivity as a function of temperature of K_3C_{60} multilayers between 5 and 100 K. We observe the transition from a semiconductor to a superconductor and discuss the data in the context of disorder and film thickness.

2. Experimental set-up

All the discussed work was carried out in a single UHV system (NEXT cluster tool [7]) with a base pressure around 5×10^{-11} mbar. The low doped silicon substrate (50 Ω cm p-type from standard stock) was prepared with a four-probe metallization pattern already in place. The measurement region consists of a square arrangement of contact lines with 200 nm probe separation. The annealing procedure of the Si(111) surface yielded a 7×7 reconstruction within the measurement region.

The C_{60} was evaporated onto the reconstructed Si surface at room temperature. The C_{60} source is a Knudsen cell operated at 600 K resulting in a rate of two monolayers (ML) per hour. These growth conditions result in well-ordered multi-layers as shown in Fig. 1. It is important to note that the growth of the e.g. 3rd layer begins before full completion of the 2nd layer and so forth (Stranski–Krastanov growth mode). A single monolayer can be prepared by thermally desorbing additional layers since the first layer is chemisorbed on the Si. In contrast, the 2nd and additional layers are just van der Waals bonded. Fig. 2 shows a high resolution STM image of the order in the 1st and 2nd ML of C_{60} on Si(111).

The films were doped by using a SAES Getters K source. We used an evaporation rate equivalent to three K atoms per C_{60} molecule in 10 min for the ML. Longer times at the same rate were used for the thicker films. This rate was established by measuring the two-probe resistance of an 8-nm-thick film on a quartz substrate during K deposition. As reported in Ref. [8] the resistance of a K_xC_{60} film goes through a minimum as the doping goes through the optimum value of $x=3$ ($x=0$ and $x=6$ are both insulating with $\rho>10^5$ Ω cm). The flux of the K source was monitored by the ion current into the -9 V biased sample using a tungsten filament in front of the getter source. Equilibration times for films around 150 nm have been reported [11] to be about 200 s. Hence, our

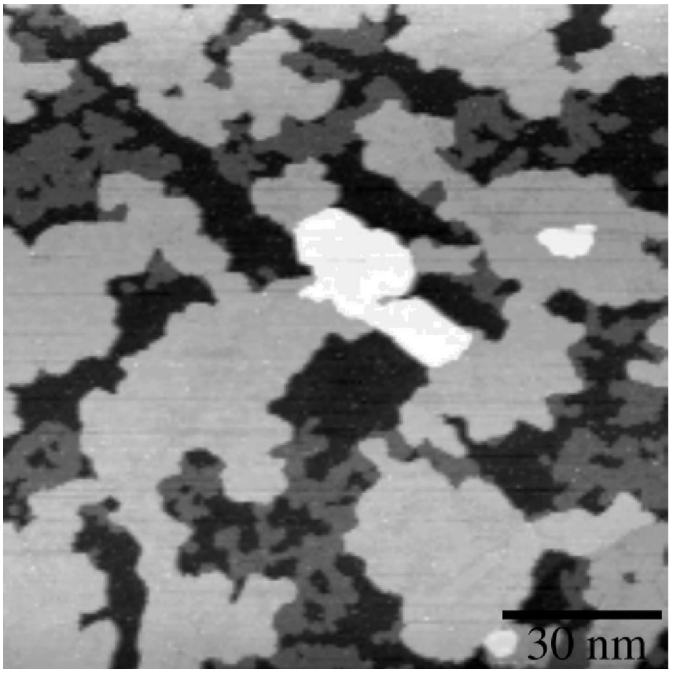

Fig. 1. First, second, third and fourth layer of C_{60} on Si(111). The lowest (darkest) level represents the first layer of C_{60}, the midlevel gray the almost complete second and third layer, and the white the fourth layer islands typical for this growth mode.

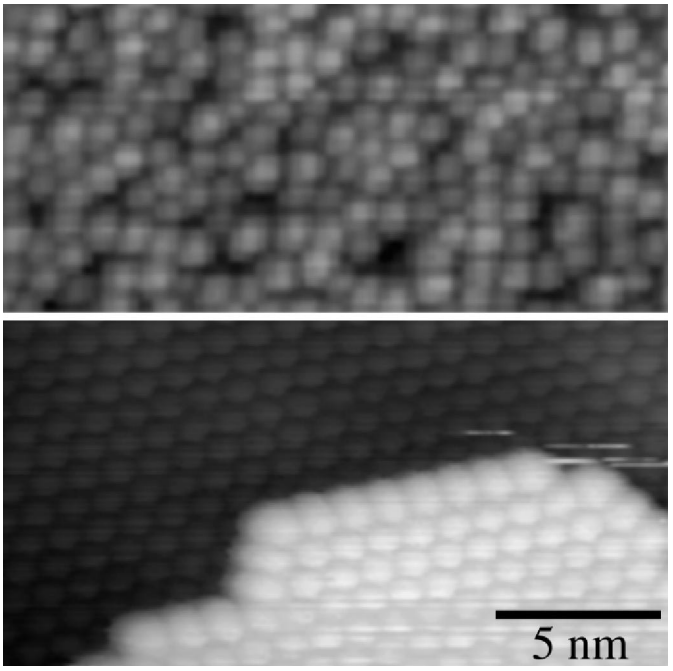

Fig. 2. STM scan of the first ML of C_{60} on Si(111) in the top of the figure, lower part shows the second and third layer. The first layer on the 7×7 reconstruction shows disorder and two domains. The second layer shows already large areas of single domain close packed structure.

films (<8 nm) should be well equilibrated directly after the slow deposition employed.

The sample was transferred to a He-flow-cryostat with a calibrated Si diode thermometer. The film resistance was measured by using the predefined metal pattern with a lock-in technique between 1.7 and 23 Hz. A current bias of 100 nA was used for the study of the temperature dependence of the resistivity. No nonlinearities were observed up to 10 μA. The parallel channel through the slightly doped substrate can be ignored below 100 K where this resistance is already in the MΩ range compared to the doped films which have a resistance of at most a few hundred kΩ.

3. Resistivity measurements

The presented data are still preliminary since all the presented data were taken on one Si(111) substrate. The measured resistance is converted into resistivity, ρ, by using the mean thickness as determined by the evaporation time, i.e. $\rho = R_{4\text{-probe}}d$. We assume that the conduction is dominated by the central region of the four probe separation, 200×200 nm^2. The results from the 6.5 ML film as shown in Fig. 3 indicate a resistivity of about 3 mΩ cm at 100 K which is consistent with the semiconducting behavior of the film. Amorphous metallic (defined as $dR/dT>0$) films have a resistivity of at best 1.5–2 mΩ cm [5] in the normal state.

The inset in Fig. 3 shows the resistivity versus temperature from 300 K down to base temperature, 5 K. The kink at 125 K can be explained by the freezing out of the conduction in the parallel path through the Si substrate.

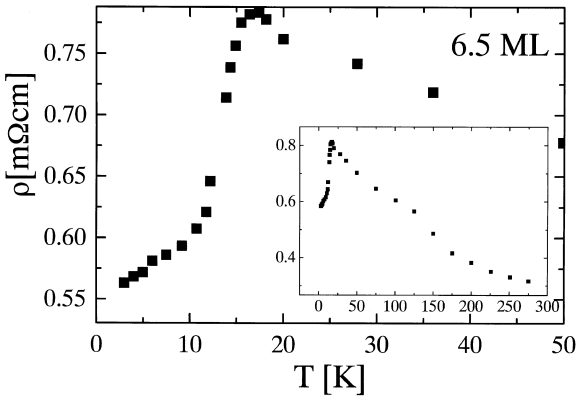

Fig. 3. Temperature dependence of the resistivity, ρ, for a film of 6.5 ML which has a mean thickness of 4.5 nm. The main plot shows the transition from semiconducting behavior to a superconducting state in a wide transition. The inset shows $\rho(T)$ from room-temperature down to base temperature of the cryostat. The kink at ≈125 K is due to freeze-out of the shunt conductance in the substrate (compare to undoped curve in Fig. 5).

For comparison the undoped ML curve in Fig. 5 shows resistance versus temperature dependence identical to the silicon since the C_{60} has a larger band-gap than the silicon. The main plot in Fig. 3 focuses on the superconducting transition. Even though the sample is doped with 3 K atoms per C_{60} we observe semiconducting behavior at temperatures above the superconducting transition. The transition is just slightly below the bulk value and fairly broad with linear shoulder at low temperature (<10 K).

Fig. 4 shows the temperature dependence of the resistivity for a 6.5 ML thick film. We observe two interesting features besides the semiconducting behavior above T_c. The value of the resistivity at 50 K is lower than that measured by other groups for the best bulk single crystal resistivities [2]. This novel ultra-thin film effect is similar to what Hebard et al. observed in their C_{60} films on thin copper layers and Tjeng et al. for K_xC_{60} on silver. Furthermore, we still observe a transition at a temperature just below the bulk T_c of the material.

A single monolayer of C_{60} on the Si(111) has been prepared by desorbing the excess C_{60} of a multi-layer as discussed above. The temperature dependence of the resistivity is shown for the doped and undoped layer in Fig. 5. As mentioned above, the resistivity of the undoped C_{60} is dominated by the shunt through the Si. Nevertheless we observe a strong shift of the conduction freeze-out temperature when the ML is doped with 3 K per C_{60}. The resistivity above the freeze-out temperature is close to the best value measured for single crystalline materials of 1.5 mΩ cm. This observation continues the trend of the very low normal state resistance of the 6.5 ML film. No transition to a superconducting state has been observed down to the base temperature of 5 K achievable in our UHV cryostat.

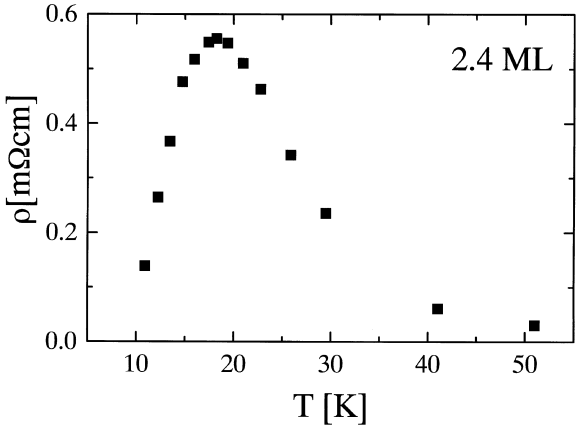

Fig. 4. Resistivity, $\rho(T)$, for a film of 2.4 ML which have a mean thickness of 1.6 nm. The plot shows the transition from semiconducting behavior to a superconducting state. Note the low resistance in the normal state compared to 1.5 mΩ cm in single crystals.

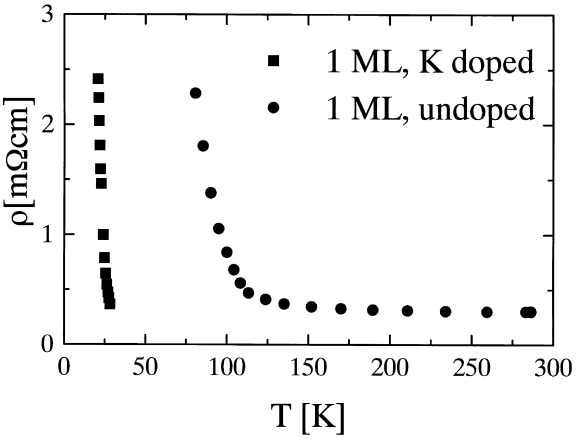

Fig. 5. Shown is the resistivity, $\rho(T)$, measured in single monolayer ($d = 0.7$ nm) of undoped C_{60} ML and of K_3C_{60} ML both on Si(111). The undoped ML shows the same conductivity as the substrate before deposition. Upon doping the freeze-out temperature goes down considerably but we do not observe a transition down to our base temperature of 5 K.

4. Discussion

The presented data could be interpreted by the assumption of a granular material with weak links between the superconducting particles. Morphology wise this is in contradiction with the film quality as shown in Fig. 1. On the other hand, if metallic properties are confined to a minimum film thickness of a few MLs then the perfectly layered film can be viewed as metallic 'grains' weakly linked by regions in the film which are below the thickness limit for metallic behavior. These 'grains' are part of the crystalline film with thickness above critical limit to be superconducting. This critical limit can be due to confinement resulting in discrete level spacing in these small islands as has been discussed for Al grains in Ref. [10]. This model would cause a semiconducting resistivity increase at low temperature before Josephson coupling would lower the film resistance. One would also expect a slowly dropping finite resistance below the transition temperature due to the distribution of tunneling length expected from the island morphology. The observation of a similar transition temperature of the 6.5 and 4.5 ML film supports a model of superconducting 'grains' with weak links rather than a disordered superconducting film. Disorder on the atomic/molecular scale should lead to a metallic normal state but lowered transition temperature [11].

The normal state resistivity could be modeled as simple thermally activated, $\rho \propto \exp(-T_0/T)$, or as weak localization, $\rho \propto \log(T)$. The latter has been successfully used to model the conduction in very disordered films [12]. Fig. 6 shows the resistivity data of the 26 ML film plotted in a way suitable for the two models. The weak localization, $\rho \propto \log(T)$ model does fit and the data are not more

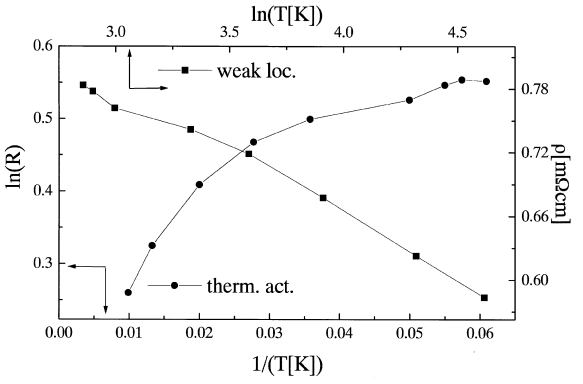

Fig. 6. The graph shows the natural logarithm of the resistivity of the 6.5 ML K_3C_{60} film versus the $1/T$ and $R \propto \ln(T)$. The first should lead to a line for thermal activation with a single activation energy. The second to a line for weak localization as successfully used for disorder films.

consistent with simple thermal activation. The same fit applied to the 6.5 ML does not yield a clear conclusion.

The lack of a transition in the single ML does not prove by any means that a monolayer cannot conduct. As shown in Fig. 2 the first layer of C_{60} on Si(111) is not well ordered in contrast to the additional layers. The semiconducting behavior of the 6.5 ML film above the transition suggests weak links. The latter film does have a completed 2nd layer and at least a percolating 3rd layer. This continuous structure should result in scattering limited metallic behavior in the normal state (high ρ but $d\rho/dT \geq 0$). Finally domain boundaries due to atomic steps in the substrate and the C_{60} ordering on the 7×7 reconstruction have to be considered. These lead to a domain structure in the doped C_{60} film which can act as a weak link.

5. Conclusion

The temperature dependence of the electrical resistivity of mono- and multi-layers of K_3C_{60} on Si(111) has been studied. A transition from semiconducting to superconducting behavior has been observed down to film thicknesses of 2.4 ML (1.6 nm). The normal state resistivity of the 2.4 and 1 ML thick films was comparable or lower than the single crystal bulk values. This is in contrast to the higher resistivity of the 6.5 ML film and the semiconducting behavior. Our preliminary data suggests that parts of the films are metallic and superconducting with a low normal state resistance. These parts of the ordered film are connected by weak links resulting in the semiconducting behavior. Further studies including detailed morphology studies and local spectroscopy on the films at low temperature are necessary to explore the novel properties of these materials.

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