Growth and characterization of potassium-doped superfulleride thin films

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Alkali-metal-doped fulleride compounds have generated great interest in the past due to the discovery of superconductivity in K$_x$C$_{60}$ ($T_c = 18$ K), Cs$_x$C$_{60}$ ($T_c = 40$ K), and mixed fulleride phases. These compounds were formed by half filling of the $t_{1g}$ (LUMO derived) band of C$_{60}$. Despite the high electron affinity of C$_{60}$, it was contended that charge transfer saturation apparently occurred at six electrons per C$_{60}$ molecule for the alkali metal-doped compounds, and early attempts were unsuccessful in filling the $t_{1g}$ (LUMO+1 derived) band and forming superfullerides (K$_x$C$_{60}$, $x > 6$). The deposition in these experiments was carried out by evaporating potassium on C$_{60}$ films at room temperature. The occupation of the $t_{1g}$ band was, however, obtained for alkaline earth metal-doped fullerides. More recently, Benning et al. and Jiang et al. altered the growth conditions by depositing potassium first on a liquid nitrogen-cooled substrate, followed by C$_{60}$ deposition. The occupation of the $t_{1g}$ band was then observed for the K-doped superfullerides in photoemission spectroscopy. Herein we draw on these earlier studies that concerned the growth of few monolayers thick superfulleride films and demonstrate the growth of 100–300 Å superfulleride films by correlating the electrical and optical properties of these compounds with their electronic structure.

Optical absorption is an important in-situ tool for characterizing these thin films. Bulk C$_{60}$ is a molecular solid, and hence the bands in the absorption spectra of C$_{60}$ thin films can be correlated to electronic bands derived directly from the molecular states of the C$_{60}$ molecule. Further, due to the similarity in the absorption spectra of various alkali-metal-doped C$_{60}$ compounds, the peaks of the spectra may be assigned to electronic transitions in the host fullerene molecule, rather than those of the dopant. Thus, the peaks in the absorption spectra of C$_{60}$, K$_x$C$_{60}$, and K$_y$C$_{60}$ have been assigned in previous publications, and the extent of electron transfer from alkali metal to C$_{60}$ and the related changes in film stoichiometry and conductivity have been explained. Our work presented here uses the growth techniques described by Jiang et al. in a high vacuum chamber with instrumentation similar to that employed by Wilson et al. to report the first determinations of electrical resistivity and optical absorption spectra of these superfulleride compounds. The compounds are identified by correlating resistivity measurements with distinct features in the absorption spectrum corresponding to the filling of the $t_{1g}$ band and $t_{1g}$ bands of C$_{60}$. We suggest the growth of two superfulleride phases occurs, a near metallic K$_x$C$_{60}$ ($x \approx 11.2$) phase and a more insulating K$_x$C$_{60}$ ($x = 8$–9) phase.
Due to the air sensitivity of the K-doped fullerides, *in situ* optical and electrical measurements were used to identify the phases. The thin films were grown on substrates that contained four 1000 Å thick silver pads evaporated on the quartz substrate prior to film deposition. The silver pads can be used as electrodes in four-point resistivity measurements of the films. For optical measurements, the chamber was equipped with a sapphire window that is transparent from 250 to 1500 nm. The absorption measurements utilized a 200 W Hg-Xe lamp as a source and the optics produced a 2\( \times \)1 in\(^2\) beam of 300–700 nm light onto the quartz substrate. Two solar cells, mounted on the sample holder, were used as detectors. UV-visible absorption spectra of the phases of interest were determined in the 300–700 nm wavelength range by depositing the thin films on a portion of the substrate such that one cell detected light passing only through the substrate, while the other cell detected light passing through the phase of interest and the substrate. The absorbance was determined from the currents of the two solar cells. The instrumentation was set up such that resistivity and optical measurements could be obtained simultaneously as a function of doping.

**III. RESULTS AND DISCUSSION**

Powder x-ray diffraction (XRD) was used to determine the quality of \( C_{60} \) films grown in our chamber. The XRD in Fig. 2 establishes that the 300 Å \( C_{60} \) films are fcc and polycrystalline with a lattice parameter of 14.2 Å and grain size of approximately 100 Å. We then grew thin films of K-doped fullerides (\( K_3C_{60} \) and \( K_6C_{60} \)) by dosing potassium on the \( C_{60} \) films as has been done earlier. No charge transfer occurred beyond the formation of \( K_6C_{60} \) under these conditions. The resistivity decrease at longer K deposition times has been attributed to unreacted metallic potassium deposited on the surface and contributing to a resistance decrease. Working on the premise that formation of higher fullerides is limited by the relatively low potassium concentrations that can be achieved at room temperature prior to compound formation, potassium was deposited on the quartz surface cooled to 200 K, followed by \( C_{60} \) deposition in a proportion such that \( K/C_{60} > 12:1 \). The surface was then annealed to 300 K for about two hours, yielding a phase labeled as \( K_xC_{60} \) which has a near metallic resistivity, as shown in Fig. 3. Metallic potassium conductivity could not be detected until the deposition of some \( C_{60} \) on the surface, which suggests that potassium grows on the quartz surface as islands rather than as a uniform layer. A possible growth model for the fulleride films is that \( C_{60} \) and K interdiffuse to form fulleride compounds that grow as polycrystalline films atop the quartz substrate. Annealing to 300 K promotes interdiffusion and brings about desorption of excess potassium from the surface. The latter is evident from the observation that for annealing temperatures lower than the K-sublimation temperature (300–325 K), the low resistivity of metallic potassium dominates the resistivity of the thin film. The presence of metallic potassium under the above conditions is also supported by the UV-visible absorption spectra. We assume that our fulleride thin films are polycrystalline since we have obtained resistivity values that match data for \( K_3C_{60} \) and \( K_6C_{60} \) grown from polycrystalline \( C_{60} \) films by the room temperature deposition of K on \( C_{60} \).

The \( K_xC_{60} \) phase formed as in Fig. 3 has a resistivity of about 9.5\( \times \)10\(^{-3} \) Ω cm, which is lower than that of insulat-
the formation of lower fulleride compounds. The points in the resistivity was monitored, as shown in Fig. 3, to detect to 400 K for points after the K\textsubscript{6}C\textsubscript{60} phase. It has been shown 290 K, and the resistivity calculations are based on the total superfulleride. All of our resistivity measurements were at 3\textsuperscript{rd} order, C\textsubscript{60} was doped at a constant rate and the resistivity was monitored, as shown in Fig. 3, to detect the formation of lower fulleride compounds. The points in this figure were generated by C\textsubscript{60} deposition on the existing K\textsubscript{12}C\textsubscript{60} phase at 200 K followed by annealing to 300 K for points between the K\textsubscript{6}C\textsubscript{60} and K\textsubscript{3}C\textsubscript{60} phases, and annealing to 400 K for points after the K\textsubscript{6}C\textsubscript{60} phase. Expected relative positions of K\textsubscript{12}C\textsubscript{60}, K\textsubscript{9}C\textsubscript{60}, and K\textsubscript{6}C\textsubscript{60} phases are marked based on the minimum resistivity denoting K\textsubscript{6}C\textsubscript{60} and the assumptions stated in the text.

FIG. 3. Resistivity of the K-doped fulleride and superfulleride phases. The K\textsubscript{6}C\textsubscript{60} phase was formed by C\textsubscript{60} deposition on K multilayers (approximately 170 Å) at 200 K, followed by annealing to 300 K until the resistance stabilised. All other points were generated by C\textsubscript{60} deposition on this K\textsubscript{6}C\textsubscript{60} phase at 200 K followed by annealing to 300 K for points between the K\textsubscript{6}C\textsubscript{60} and K\textsubscript{3}C\textsubscript{60} phases, and annealing to 400 K for points after the K\textsubscript{6}C\textsubscript{60} phase. The UV-visible absorption spectrum of this K\textsubscript{6}C\textsubscript{60} phase is shown in Fig. 4, and compared with that of thin films of other fulleride compounds. The peaks may be assigned using the schematic of induced electronic transitions shown in Fig. 5, indicating the expected absorptions (solid arrows) and bleaches (dashed arrows) upon occupation of the \(t_{1u}\) and \(t_{1g}\) levels. The spectra for K\textsubscript{6}C\textsubscript{60} and K\textsubscript{8}C\textsubscript{60} show bleaching of the band corresponding to the \(g_x \rightarrow h_g \rightarrow t_{1u}\) transition seen for C\textsubscript{60} at 360–370 nm. It has been demonstrated by Wilson et al.\textsuperscript{16} that this bleaching is related to the filling of the \(t_{1u}\) band. Based on this, it may be argued that filling of the \(t_{1g}\) band to form the superfulleride phase should be accompanied by bleaching of the band corresponding to the \(h_{u} \rightarrow t_{1g}\) transition, which occurs for K\textsubscript{8}C\textsubscript{60} in the broad region between 500 and 550 nm.\textsuperscript{15–17} For K\textsubscript{8}C\textsubscript{60} the band centered at 460 nm has been assigned\textsuperscript{17} to three distinct transitions. These are the \(t_{1u} \rightarrow h_{g}\) transition, which has been moved down in energy from its expected molecular value, and the \(h_{u} \rightarrow t_{1g}\) and the \(t_{1a} \rightarrow t_{2g}\) transitions that give rise to the broad shoulder toward higher wavelengths. Comparing the spectra of K\textsubscript{6}C\textsubscript{60} and K\textsubscript{8}C\textsubscript{60} in Fig. 4, the notable features of the former are the narrowing of the peak at 460 nm (\(t_{1u} \rightarrow h_{g}\) transition) and the continued bleaching of the \(g_x \rightarrow h_g \rightarrow t_{1u}\) transition seen in the difference spectrum of Fig. 6 as a negative peak at about 530 nm (2.35 eV), consistent with the energy band

of only 2.3%\textsuperscript{20} Similarly, it is expected that the phase transformation to form superfullerides should involve only a small volume change. This also concurs with the sodium superfulleride (Na\textsubscript{11}C\textsubscript{60}) structure proposed by Yildirim et al.\textsuperscript{21} It should be noted, however, that the resistivity of thin films of doped fullerenes is dependent on grain size of the phase being grown.\textsuperscript{19} While the grain size of the C\textsubscript{60} film in these experiments is known from x-ray diffraction (100 Å), that of the fulleride and superfulleride phases is not known. Hence variations from the resistivity values reported here may be found due to the dependence of the grain size on the technique used for the preparation and growth of the superfulleride phases. The resistivity error bars in Fig. 3 include an accounting for thickness errors and electrical measurements errors. The horizontal error bars are based on comparison of the measured C\textsubscript{60} thicknesses using the quartz microbalance with measurements from ellipsometry. In all cases the error bars represent the maximum possible error in the data and include estimates of systematic errors derived from independent measurement techniques.

In addition, Fig. 3 shows the expected relative positions (dashed lines) of K\textsubscript{12}C\textsubscript{60}, K\textsubscript{9}C\textsubscript{60}, and K\textsubscript{6}C\textsubscript{60} phases based on the minimum resistivity in the curve assigned to K\textsubscript{3}C\textsubscript{60}. The stoichiometry is determined by assuming that the change in lattice parameter on formation of the various phases is negligible and that no K desorption occurs during annealing. If the thin films contain only a single phase of doped fulleride/superfulleride, then the indicated phases would be formed as shown. This prediction of the conditions for forming the K\textsubscript{6}C\textsubscript{60} phase agrees very well with the cusp characteristic of the K\textsubscript{6}C\textsubscript{60} phase.
assignment for this transition from photoemission data for the superfullerides. These results, taken along with the doping resistivity data of Fig. 3, confirm the growth of a superfulleride phase $K_x C_{60}$, $x > 6$.

We can provide some justification for labeling several of these films to be comprised of single homogenous phases. As discussed earlier, the overall stochiometry of these phases was indicated in Fig. 3. The resistivity was attributed to a single phase of fulleride/superfulleride, but in reality it could result from a mixture of fulleride/superfulleride phases and even some retained excess potassium that is not metallic but partially oxidised. However, in studies comparing bulk and thin film potassium fullerides ($K_x C_{60}$), Murphy et al. determined that a continuous variation of $x$ was obtained for the latter as opposed to discrete $x$ values of 0, 3, 4, and 6 for the former. Further, they conclude that low temperature film doping can produce “metastable” homogenous compositions. Also, Jiang and Koel have demonstrated that K and $C_{60}$ deposition at substrate temperatures as low as 100 K is sufficient to form the superfulleride phase, suggesting that interdiffusion of K and $C_{60}$ is high at low temperatures. Hence, we believe that a more or less homogeneous superfulleride phase that may be continuously doped with $C_{60}$ to form the subsequent lower fulleride phases are obtained for all the low-temperature film doping experiments reported herein.

Based on the above arguments and the stoichiometries shown in Fig. 3, we propose formation of the superfulleride phase $K_x C_{60}$ with $x \approx 11.2$. A phase with a similar stoichiometry and with fewer than 12 electrons accepted per $C_{60}$ molecule was observed by Maxwell et al. and predicted to have metallic behavior based on emission at the Fermi energy in photoemission spectra. We carried out a number of experiments searching for a more insulating phase with a higher K stoichiometry, and we have no evidence for the
identified a C$_{60}$ characteristic cusp for K$_x$C$_{60}$. The UV-vis spectrum of a other phase of K$_x$C$_{60}$ corresponding to the phase where the plateauing begins ($x \approx 8.3$), and this spectrum is quite different from that of K$_6$C$_{60}$ or tional filling of the IV. CONCLUSIONS ($x \approx 8.3$) is shown in Fig. 7. An unusual feature apparent from Fig. 3 is that upon C$_{60}$ doping, the rapidly increasing resistivity values beyond K$_x$C$_{60}$ ($x \approx 11.2$) plateau much before the formation of the characteristic cusp for K$_x$C$_{60}$. The UV-vis spectrum of a phase where the plateauing begins ($x \approx 8.3$) is shown in Fig. 7, and this spectrum is quite different from that of K$_x$C$_{60}$ or K$_y$C$_{60}$. The main peak at 450 nm appears to have a shoulder corresponding to the $h\rightarrow t_{1g}$ transition, suggesting only partial filling of the $t_{1g}$ band and the possible presence of another phase of K$_x$C$_{60}$ with $x \approx 8.9$. Benning et al.$^{11}$ have identified a C$_{60}^{d_{5h}}$ state based on photoemission results which may correspond to this phase, especially because it is also expected to be insulating. Hence, based on the above discussion, we contend that two superfulleride phases, a near-metallic K$_x$C$_{60}$ ($x \approx 11.2$) phase and a more insulating K$_x$C$_{60}$ ($x \approx 8.9$) may be formed.

IV. CONCLUSIONS
The growth of thin films ($100-300$ Å) of potassium doped superfullerides has been demonstrated. The first determinations of the electrical resistivity and optical absorption spectra of these compounds have been presented. Growth conditions for formation of these compounds have been derived by correlating electrical resistivity with distinct features in the absorption spectrum corresponding to the filling of $t_{1u}$ and $t_{1g}$ bands of C$_{60}$. Based on electrical and optical properties of the superfulleride phases, the presence of two distinct phases, K$_x$C$_{60}$ with $x \approx 11.2$ and K$_x$C$_{60}$ with $x \approx 8.9$, is suggested.

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