Anomalous suppression of the transition temperature of superconducting nanostructured honeycomb films: Electrical transport measurements and Maekawa-Fukuyama model

Deepak K. Singh,[1,*] Sigfrid Yngvesson,[2] Thomas P. Russell,[3] and Mark T. Tuominen[1,†]
[1]*Department of Physics, University of Massachusetts, Amherst, Massachusetts 01003, USA*
[2]*Department of Electrical Engineering, University of Massachusetts, Amherst, Massachusetts 01003, USA*
[3]*Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003, USA*
(Received 2 July 2007; revised manuscript received 17 December 2007; published 16 May 2008)

We report electrical transport measurements made on thin superconducting niobium films perforated by an etched array of nanoscopic holes. The hole diameter in these "honeycomb" network films is comparable to the coherence length of the parent superconducting material. A series of 12 films, with varying hole depths, were measured. As the film thickness is decreased, an unusually large reduction of transition temperature is observed for the honeycomb films as compared to plain etched films of similar thicknesses. We report on a T_c reduction in superconducting network films that is not due to an applied magnetic field. These observations are in contrast to previous reports based on Ginzburg-Landau theory analysis, which does not allow for any change in the transition temperature for perforated films in comparison to plain films. The Maekawa-Fukuyama (MF) model for two-dimensional (2D) superconductors is used to fit the sheet resistance data. The MF-2D model fits very well to the lightly etched samples, but an anomaly in T_c reduction is observed for heavily etched samples. These deviations are analyzed on the basis of change in dimensionality using the Aslamozov-Larkin model.

DOI: 10.1103/PhysRevB.77.174512 PACS number(s): 74.78.Na, 74.62.Dh, 73.63.−b

I. INTRODUCTION

Patterning a superconducting film into a multiply connected network yields a system with interesting complexity. However, the details of the behavior depend greatly on the characteristic size scale of the patterning.[1] Utilizing Ginzburg-Landau (GL) theory, previous works[2–5] on patterned niobium films suggest no change in transition temperature, in the absence of a magnetic field, for artificially patterned superconducting film as compared to plain films of the same thickness. In the presence of a field, the transition temperature for a perforated "honeycomb" superconducting film shows a different dependence on the field than a plain film of the same thickness.[6] This is consistent with the GL theory irrespective of the patterned holes being blind or open.[1] Previous research was performed on superconducting honeycomb films having a characteristic length scale larger than the coherence length of the parent superconducting material. If the honeycomb film thickness as well as the diameter of the perforated holes is comparable to the coherence length of the superconducting material, then the microscopic superconducting character itself is changed and the experimental observations must be analyzed using the microscopic theory of superconductivity. For thin superconducting films, the transition temperature decreases as the film thickness is reduced because of weak localization,[7] suppression of electron-phonon coupling constant (α),[8,9] or broadening of the superconducting energy gap edge.[10] As the film thickness is reduced, disorder increases, and as a result, the Coulomb repulsion and electron-phonon interaction both increase.[11] But after a certain minimum value of thickness, the Coulomb repulsion interaction becomes so large that it outweighs the increase in electron-phonon interaction, which becomes saturated as the film thickness is decreased. For a highly disordered system, in thin granular films, the electron-phonon interaction starts to decrease after the saturation value. This reduces the value of effective coupling interaction[12] λ-μ^*, and hence the superconducting order parameter Δ decreases. Since the transition temperature T_c for superconducting films is directly related to Δ, the transition temperature decreases also. A second important physical phenomenon to consider is the localization of density of states in the grains. As the granular film becomes thinner, material grains of the film become weakly connected. This results in weak localization. In the case of strong enough disorder of a thin film, the electron-electron interaction increases significantly and thus the electronic states are strongly localized, which also results in a metal-insulator transition (MIT).[13] Previous research works[14,15] on thin amorphous or granular superconducting films suggest that the combined effects of these two mechanisms, localization and Coulomb interactions, results in a substantial reduction of T_c as a function of increasing sheet resistance (R_s) or decreasing thickness of films. In this paper, we present the results of experimental studies of superconductivity in nanoscale-patterned Nb films (also called superconducting honeycomb films), where nanoscale-patterned holes act as scattering centers analogous to doped impurities in amorphous thin superconducting films. The honeycomb films exhibit a strong reduction in T_c as compared to plain unpatterned films of similar thicknesses and etched under similar conditions. For example, in one case, the reduction in transition temperature for 30-s etched plain film of thickness 6 nm, as compared to original film of 10 nm thickness, is ~0.04 K. On the other hand, the reduction in transition temperature for 105-s etched honeycomb film, also 6 nm thick and fabricated from original 10-nm-thick film, is 1.29 K. In the following fabrication section, it is explained how 30-s etched plain film and 105-s etched honeycomb film are of similar thicknesses. This observation is a significant deviation from previous experimental and theoretical results on patterned superconducting films.

II. FABRICATION PROCEDURE

The honeycomb films are fabricated using a thin nanoporous polymer template, derived from a diblock copolymer film, as a reactive ion etch mask on a 10-nm niobium thin sputtered film. The diblock copolymer P[S-b-MMA] consists of two chemically distinct homopolymers joined to each other at one end with a covalent bond and capable of microphase separation because of immiscibility of the polymer blocks. A microphase-separated diblock copolymer film can take various forms from spherical to cylindrical to lamellar, depending upon the volume fraction of each block,[16] and forms a periodic pattern. For our work, we follow a procedure outlined in earlier work.[17] We use a 66-kdalton-molecular-weight diblock copolymer with a volume fraction of the PS (PMMA) at 70% (30%) to obtain a hexagonal array of PMMA cylinders in a PS matrix. For this molecular weight, the average diameter of a PMMA cylinder is 13 nm and the center-to-center distance between two cylinders is 28 nm, which is in good agreement with prior work.[18] To remove the PMMA cylinders, the sample is exposed with 3 J/cm^2 of UV (254 nm wavelength) and then rinsed in pure acetic acid for 7 min, followed by a 5-min rinse in distilled water in an ultrasonic bath. This results in a 36-nm-thick PS film perforated by a hexagonal array of 13-nm pores on top of Nb film with native oxide layer. After fabricating a nanoporous template on top of Nb film, reactive ion etching is used to etch the honeycomb geometry into the Nb film. The reactive ion etching is performed using low-pressure CF_4 gas at a chamber pressure of 84 mTorr and 52 W power. The substrate was voltage biased during the etching to facilitate anisotropic etching perpendicular to the surface. Organic residues are removed by cleaning the sample in sulfuric acid at 50 °C for 1 min. Before etching the actual samples for honeycomb films fabrication, the etching rate is calibrated for the thickness of original Nb film. It is found that the etching rate for plain Nb is 1 nm in 7.5 s, so the Nb film is destroyed after 75 s of etching. Coincidentally, this is also the time required to completely etch the polymer mask. This means any additional etching results in a multiply connected honeycomb system with decreased film thickness. For comparison purposes, plain Nb films are also etched under identical conditions and for a similar amount of times. It is important to underscore that a plain Nb film etched for 15 s has the same thickness as an etched honeycomb film etched for 90 s. This is because the honeycomb film is protected by the diblock mask for times up to 75 s. Since this is tricky to understand, therefore, we have drawn a schematic description of this procedure in Fig. 1. In this schematic figure, we can clearly see that the honeycomb films etched for small amount of time (15 s., 30 s. etc.) has the thickness of 10 nm, but longer etched (75 s or more) honeycomb films are thinner than 10 nm. As the diblock mask pore diameter is 13 nm, the hole diameters of lightly etched honeycomb films are also of the same value, but in the case of longer-etched honeycomb films, the hole diameters are larger than this value because of undercuts during the etching process.[19,20] After 140 s of reactive ion etching for honeycomb films, the multiply connected Nb network is destroyed (also confirmed by electrical transport measurements discussed below). A total of 12 Nb honeycomb films were fabricated, having increasing hole depths and decreasing thicknesses, by varying the etching time from 5 s to 140 s. Atomic force microscope (AFM) images of selected honeycomb films are shown in Fig. 2.

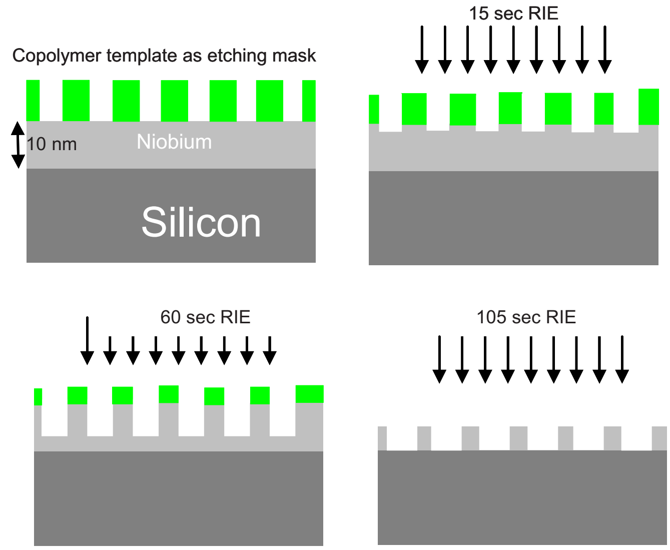

FIG. 1. (Color online) Schematic description, in 2D, of “honeycomb” film fabrication for different etching times. As we can see in this schematic picture, the thickness of the lightly etched honeycomb film is same as the original film (10 nm), but as the etching time is increased, holes become deeper as well the constriction (film connecting two neighboring holes) gets thinner. Eventually after certain amount of time, the holes are etched all the way (open holes) through and create a multiply connected system of lower thickness than the original film.

III. ELECTRONIC TRANSPORT MEASUREMENTS

Electrical transport measurements are performed using four probe techniques and an autobalancing resistance bridge for all the samples. For comparison purposes plain Nb films of comparable thicknesses, as mentioned in the previous paragraph, are also measured. Sheet resistance, R_s, data for both honeycomb and plain Nb films are plotted as a function of temperature in Fig. 3.[21] We can see in Fig. 3 that the sheet resistance value for both plain Nb films and honeycomb films are much smaller than the quantum resistance value ($R_Q=\frac{h}{4e^2}=6.4\ \text{k}\Omega$) below which superconductivity is possible. The 50% value of the 8-K normal resistance on $R_s(T)$ curves is used as a convention to determine the superconducting transition temperatures for all the samples. According to Fig. 3, the superconducting transition temperature for the unetched original plain Nb film (the parent film) is 6.89 K, but after fabricating diblock template mask on top of Nb surface, we observe a substantial reduction to $T_c=3.52$ K. It is an interesting observation worthy of further experimental investigation to be pursued in future work, involving details of the polymer-metal interaction. In this report we will focus on the physics of superconducting honeycomb films. As we can see in Fig. 3(b), the transition temperatures for etched

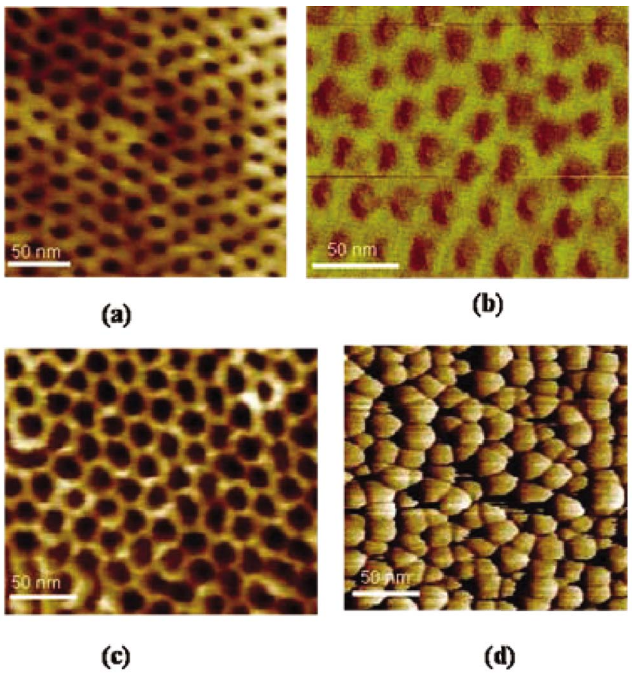

FIG. 2. (Color online) AFM images of diblock template and honeycomb films (before imaging, samples are cleaned in sulfuric acid at 70° centigrade). (a) Diblock template, (b) 15-s etched sample, (c) 105-s etched sample (note that constrictions are getting thinner, as discussed in the text, possibly because of undercuts), and (d) 140-s etched sample (complete etching results in the exposure of a Si wafer).

plain Nb films reduce gradually as the etching time is increased and eventually superconductivity is destroyed for the sample etched for 75 s. For superconducting honeycomb samples we observe a characteristically different behavior in T_c reduction. Since the honeycomb films are protected by a polymer mask (as shown in Fig. 1) until 75 s of etching time, the thickness of the these honeycomb films (etched up to 75 s) remains intact at 10 nm, but the hole depth increases. A transition from "blind-hole" honeycomb film, a simply connected system, to "open-hole" honeycomb film, a multiply connected system, occurs after 75 s of etching time. Further etching results in open honeycomb films of lower thicknesses than the original film. The thicknesses of honeycomb films etched for more than 75 s reduce in a similar way as in the case of plain etched film. Thus a 90-s etched honeycomb film has the same thickness as a 15-s etched plain film. The superconducting transition temperatures for honeycomb films is reduced gradually up to 75 s of etching time, but for further etching a *substantial* reduction is observed.

In Fig. 4 we have plotted the variation of normalized transition temperature, $\frac{T_c}{T_{c0}}$, as a function of etching time. Here T_c is the transition temperature of the film and T_{c0} is the transition temperature of the respective unetched film. In the case of plain Nb film the value of T_{c0} is 6.89 K, while for honeycomb film it is 3.52 K. Figure 4 demonstrates that two superconducting systems of similar thicknesses behave differently as they become thinner. As we see in Fig. 4, there is a much larger relative reduction in the transition temperatures for longer-time-etched honeycomb films as compared to

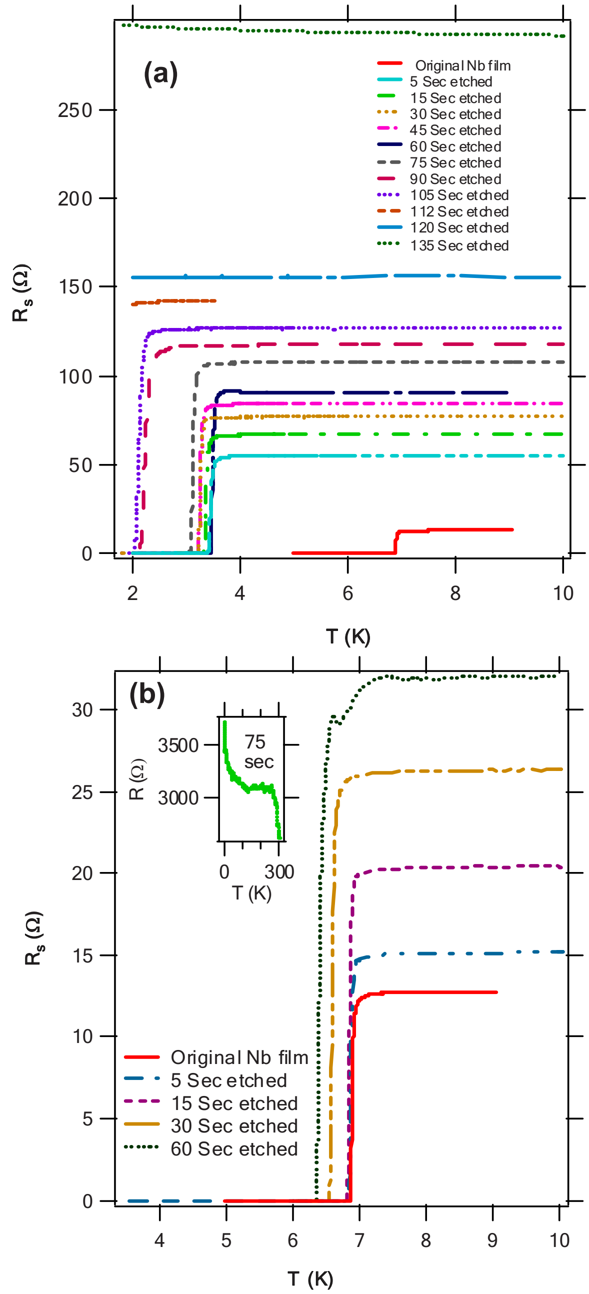

FIG. 3. (Color online) Sheet resistance data for different time etched samples. (a) Different time etched honeycomb films. This plot clearly shows that as the sheet resistance value increases, transition temperature decreases. (b) For comparison purposes, plain Nb film sheet resistance data are also plotted. In the inset, sheet resistance data for 75-s etched plain Nb film is shown. As we can see here superconductivity is destroyed in plain Nb film after 75 s of etching time.

plain etched Nb films. For a plain Nb film etched for 15 s, the reduction in temperature is of about 0.02 K as compared to original Nb film, while for the comparable honeycomb film etched for 90 s it is about 1.28 K. This is in contrast to Ginzburg-Landau theory,[1] which predicts that, whether they be multiply connected or simply connected, two films of the same thickness will have the same transition temperature. Table I emphasizes the observations of reduction in T_c for

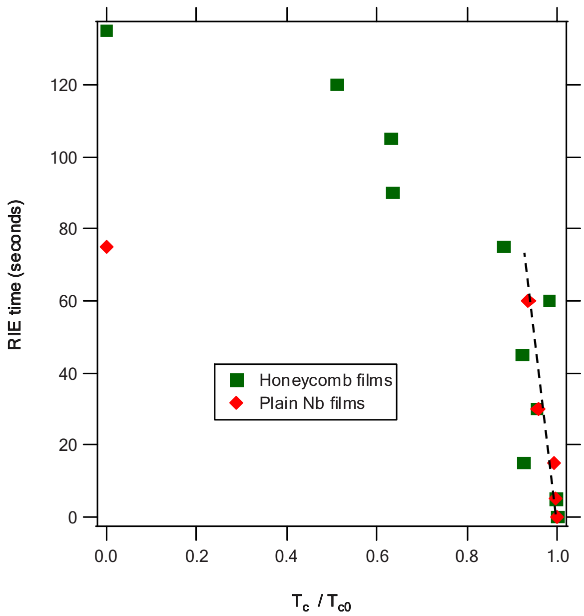

FIG. 4. (Color online) The variation of normalized transition temperature as a function of etching time for both plain Nb films and honeycomb films. As the etching time increases, sample thickness decreases linearly (see text). In this figure we observe two very different behaviors in T_c reduction for films of similar thicknesses, in the absence of magnetic field. Just a guide to the eye, the dashed line shows a linear variation of T_c with increasing etching time for plain Nb film.

honeycomb films as compared to plain Nb films of *similar thicknesses*.[22] Honeycomb films etched for longer times show substantial transition temperature differences as compared to plain films. For thin and granular plain Nb films it is well established that weak localization is largely responsible for the suppression of transition temperature as the film thickness is decreased.[7] The weak localization effect is usually exhibited by the $1/d$ dependence of T_c and also the magnetoresistance ratio $\Delta R/R \sim 10^{-4}$ in a large field region. We also observe a linear variation of the transition temperature as a function of reducing thickness for plain Nb films, as shown in Fig. 4 by a dashed line. In Fig. 3, another noticeable feature is the jump in resistance, before making the superconducting transition, for samples etched for 60 s of both honeycomb and plain Nb films. Interestingly this behavior does not occur for any other etched sample. Nonetheless, we are specifically interested in understanding the mechanism behind the T_c reduction in honeycomb films.

TABLE I. In this table, T_c is the transition temperature of the specified film while T_{c0} is the transition temperature of the parent film; in the case of plain films, it is the transition temperature of original Nb film (6.89 K), while in the case of honeycomb films it is the transition temperature of unetched Nb film with diblock on top (3.52 K).

Thickness of the film	$\Delta T_c = T_c - T_{c0}$ (honeycomb films)	$\Delta T_c = T_c - T_{c0}$ (plain Nb films)
10 nm	0.41 K (75 s)	0 K (unetched)
8.0	1.28 K (90 s)	0.02 K (15 s)
6.0 nm	1.29 K (105 s)	0.038 K (30 s)

IV. MAEKAWA-FUKUYAMA MODEL

Weak localization is the mechanism predominantly attributed to the suppression of the transition temperature in thin Nb films of two dimensions. However, in some cases, especially in thin amorphous or grainy superconducting films or films with impurities, previous research works[13,14] suggest that a combined effect of localization and Coulomb interactions results in a sharp reduction of T_c as a function of increasing sheet resistance R_s or decreasing thickness of films. In these cases the Maekawa-Fukuyama (MF) model[23] has been a more accurate model for explaining the T_c reduction as a function of increasing sheet resistance. The only limitation is that it is valid only for two-dimensional (2D) superconductors. For a 2D superconductor, the MF perturbation theory calculations result in

$$\ln\left[\frac{T_c}{T_{c0}}\right] = -\frac{1}{2}\frac{g_1 N(0)e^2 R_s}{2\pi^2\hbar}\left[\ln\left\{5.5\frac{\xi_0}{l}\frac{T_{c0}}{T_c}\right\}\right]^2 - \frac{1}{3}\frac{g_1 N(0)e^2 R_s}{2\pi^2\hbar}\left[\ln\left\{5.5\frac{\xi_0}{l}\frac{T_{c0}}{T_c}\right\}\right]^3, \quad (1)$$

where R_s is the sheet resistance of 2D superconductors and $g_1 N(0)$ is the effective coupling constant. In the above equation the first term is due to the reduction of density of states as a result of localization and second term is the vertex correction to the electron-electron interaction. The only fitting factor in this model is the effective coupling constant $g_1 N(0)$. The calculated coherence length value, using H_{c2} data, for plain Nb film is $\xi_0 \approx 8.1$ nm.[24] Therefore, for an original thickness of 10 nm, etched films are 2D or lower-dimensional systems from the superconducting dimensionality point of view. We have investigated the changes in the effective dimensionality of honeycomb films, as a function of etching time, to understand the increasing temperature width of superconducting transitions and are discussed below later. In Fig. 3(a) we also observe the increasing sheet resistance values as the film thickness decreases for honeycomb films (as a result of increased etching time) and also suppression of the transition temperature. In the case of honeycomb films, holes act as scattering centers for transport electrons, analogous to a superconducting film with impurities. As discussed above in the Maekawa-Fukuyama equation, the first term on the right-hand side is due to the correction to the density of states and the second to enhancement of the Coulomb repulsion between electrons due to nanoscale patterning plus ion etching damage in the honeycomb films. The value of $g_1 N(0)$ may be compared with that of the screened Coulomb interaction for strongly coupled superconductors,[25] which gives $g_1 N(0) \sim 1$. The zero-temperature coherence length for plain sputtered Nb, verified for a plain Nb film with the polymer template on top, is of the order of 8 nm, as mentioned above, and the calculated value for elastic mean free path is of the order of ~ 1 nm. The elastic mean-free-path length in the dirty limit is calculated using the formula

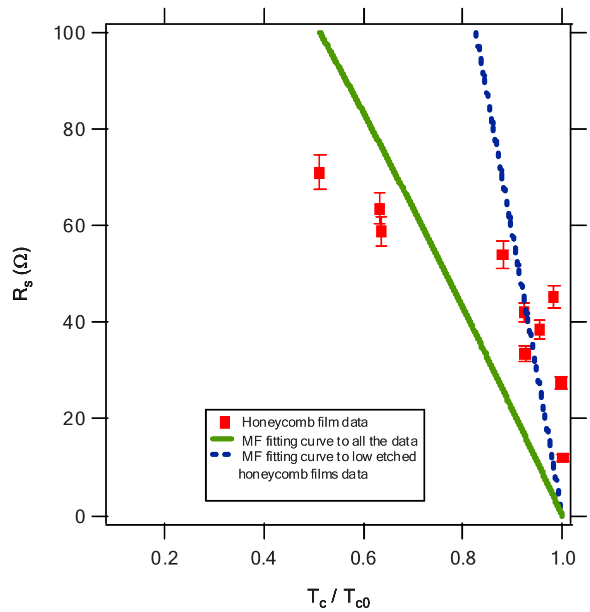

FIG. 5. (Color online) Maekawa-Fukuyama 2D model fitting to sheet resistance data for honeycomb films. As we can see in this figure the MF-2D model (green, solid gray, curve) does not fit well to the all data points. But if we fit the MF-2D model to the lightly etched honeycomb films data, then, as we can see in this figure (blue, dashed gray, curve), a very good fitting is obtained. The fitting value of the coupling constant, in this case, is 0.8.

$\xi_0 \sim [\xi(0)l]^{1/2}$, where $\xi(0) \sim 40$ nm is the coherence length for pure crystalline Nb.[26] The ratio $\frac{\xi_0}{l}$ therefore is expected to be around 8, and hence the only remaining parameter is the effective coupling constant $g_1 N(0)$, which is expected to be of the order of unity. In Fig. 5, we have plotted $\frac{T_c}{T_{c0}}$ vs R_0 for honeycomb films. Data has been fitted, in Fig. 5, using MF-2D theory. As we can see in that figure, fitting (green curve) is not good for all the data points and the obtained fitting value is an unreasonably small value of 0.108. In the strong-coupling limit, as in this case, one would expect the fitting value to be of the order of 1.0. On the other hand, if we fit the data for lightly etched honeycomb films (blue curve), then we get a fitting value of $g_1 N(0) \sim 0.8$, which is quite reasonable. This reflects that due to nanoscale patterning, in honeycomb films etched for short times, an anomalous diffusive behavior occurs that reduces the electron screening via exchange correction, thereby enhancing the Coulomb interaction parameter and reducing the effective interaction parameter. One reasonable explanation for the deviation of the MF-2D fitting curve from the data for honeycomb films etch for longer times may be a further reduction in the effective dimensionality of the honeycomb films with increasing etching times. In such a case, the MF model, which is strictly valid only for 2D superconductors, is no longer applicable. However, other authors[14] have suggested higher-order positive corrections to the theory for further increasing values of R_s.

V. DISCUSSION

To verify the assumption of changing dimensionality, we use the Aslamozov-Larkin model[27] to determine the superconducting dimensionality of the film. For this purpose we have plotted conductivity (σ) vs scaled temperature $[(T - T_C)/T_C = t]$ for plain films and honeycomb films in Fig. 6. Data are fitted using the Aslamozov-Larkin (AL) model. In the AL theory, a log-log relation between conductivity and temperature is given by[28,29]

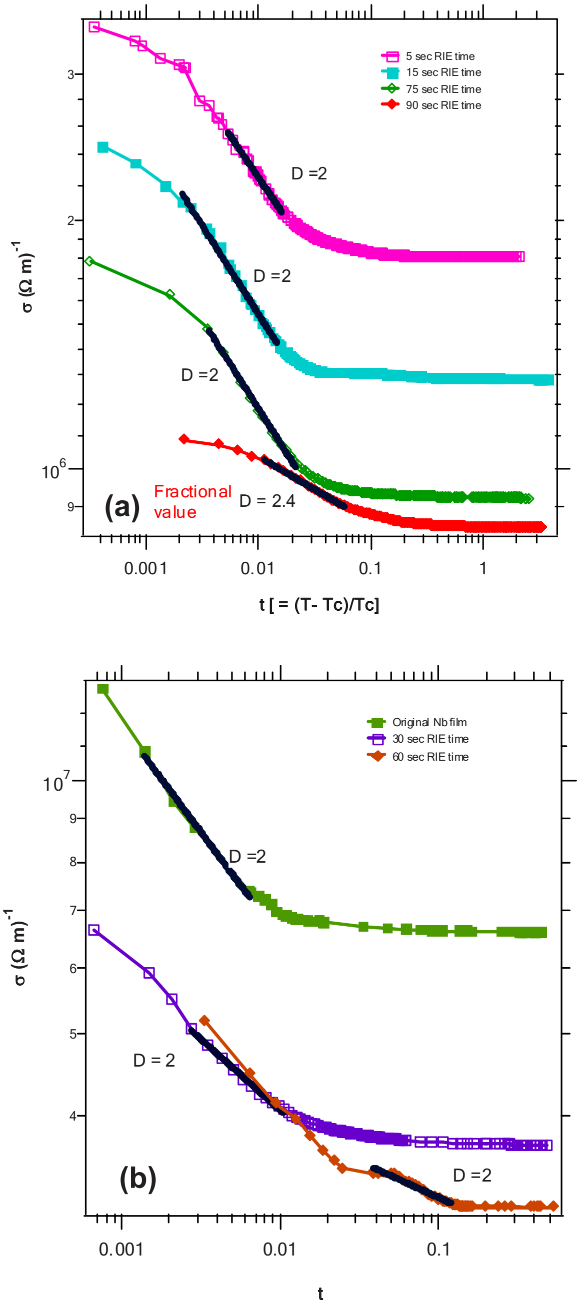

FIG. 6. (Color online) Fitting to the excess conductivity data using the Aslamozov-Larkins model. As we can see in this figure, the superconducting dimensionality of the original film is 2D, which was expected because the thickness of the Nb film is of the order of coherence length for the superconductor. (a) In the case of honeycomb film, dimensionality changes from 2D to a fractional value for increased etching time. (b) In the case of plain Nb film, dimensionality does not change.

$$\sigma = (a + bT)^{-1} + c\left(\frac{T - T_c}{T}\right)^{-(\varepsilon+1)}, \quad (2)$$

where a, b, and c are fitting constants and ε is the fitting power for excess conductivity. The first part on the right-hand side is background conductivity and is subtracted from the data before doing the actual fitting. In the AL model, the parameter ε is related to the fluctuation dimensionality D by

$$D = 4 - 2\varepsilon. \quad (3)$$

After fitting the data using AL model, we see that for lightly etched samples ε is around 0.9 (with an estimated error of about ± 0.1) and therefore the value of D is about 2. For heavily etched samples (for instance, 90-s etched honeycomb film) the value of ε reduces to 0.78 and hence increasing the dimensionality D to a fractional value of 2.4. This is a very strange observation as one would expect to observe lower dimensionality with reducing thickness of the film. On the contrary, we see not only the higher dimensionality of the system, but also a fractional form. This dimensionality analysis accounts for the departure of the data from the MF-2D model, but it does not explain in detail the anomalous reduction in transition temperature.

In summation, the combined effects of weak localization and interaction effects reduces the transition temperature of honeycomb films etched for short times. One possible explanation for substantial reduction in T_c for honeycomb films etched for long times may be the magnetic interactions, induced by transport current, between closely spaced open holes, as described by Bezryadin *et al.*[1] Nanoscopic open holes, in this case, can be thought of as cylinders of very small dielectric constants. Here it is noteworthy to mention that for heavily etched honeycomb films, the thickness of the film is smaller than the magnetic penetration depth and honeycomb wall thickness is smaller the original masked spacing (Fig. 2). In such a case, the induced magnetic moments across the open holes start interacting because of the close spacing and can create an effect analogous to an applied magnetic field, reducing the transition temperature. In lightly etched honeycomb films, this phenomenon is not very pronounced because of the underlying connecting film and ample separation between holes. Clearly detailed theoretical investigations are needed to fully understand the behavior of this regime of nanostructured superconducting networks.

ACKNOWLEDGMENTS

This project was supported by NSF Grants No. DMR-0531171 and No. DMR-0306951 and MRSEC.

*Present address: Dept. of Physics, Massachusetts Institute of Technology, Cambridge, MA 02139, USA.
†Corresponding author. tuominen@physics.umass.edu

[1] A. Bezryadin, Yu. N. Ovchinnikov, and B. Pannetier, Phys. Rev. B **53**, 8553 (1996).
[2] A. Bezryadin and B. Pannetier, J. Low Temp. Phys. **98**, 251 (1995).
[3] V. A. Schweigert and F. M. Peeters, Phys. Rev. B **60**, 3084 (1999).
[4] M. D. Stewart, Jr., Zhenyi Long, James M. Valles, Jr., Aijun Yin, and J. M. Xu, Phys. Rev. B **73**, 092509 (2006).
[5] R. Rammal, T. C. Lubensky, and G. Toulouse, Phys. Rev. B **27**, 2820 (1983).
[6] U. Welp, Z. L. Xiao, J. S. Jiang, V. K. Vlasko-Vlasov, S. D. Bader, G. W. Crabtree, J. Liang, H. Chik, and J. M. Xu, Phys. Rev. B **66**, 212507 (2002).
[7] J. H. Quateman, Phys. Rev. B **34**, 1948 (1986).
[8] R. C. Dynes, A. E. White, J. M. Graybeal, and J. P. Garno, Phys. Rev. Lett. **57**, 2195 (1986).
[9] A. F. Hebard and M. A. Paalanen, Phys. Rev. B **30**, 4063 (1984).
[10] A. E. White, R. C. Dynes, and J. P. Garno, Phys. Rev. B **33**, 3549 (1986).
[11] M. Strongin, R. S. Thompson, O. F. Kammerer, and J. E. Crow, Phys. Rev. B **1**, 1078 (1970).
[12] G. M. Eliasberg, Sov. Phys. JETP **11**, 696 (1960).
[13] Y. Imry, *Introduction to Mesosscopic Physics* (Oxford University Press, Oxford, 1997), Chap. 2.
[14] H. Raffy, R. B. Laibowitz, P. Chaudhari, and S. Maekawa, Phys. Rev. B **28**, 6607 (1983).
[15] J. M. Graybeal and M. R. Beasley, Phys. Rev. B **29**, 4167 (1984).
[16] F. S. Bates and G. H. Fredrickson, Phys. Today **52**(2), 32 (1999).
[17] T. Xu, H. C. Kim, J. DeRouchey, C. Seney, C. Levesque, P. Martin, C. Stafford, and T. P. Russell, Polymer **42**, 9091 (2001).
[18] M. W. Matsen and F. S. Bates, Macromolecules **29**, 7641 (1996).
[19] J. A. Bondur, J. Vac. Sci. Technol. **13**, 1023 (1976).
[20] Undercuts during the etching process also affect the overall etching thicknesses for heavily etched honeycomb films.
[21] There is possibility of a very small measurement error in measuring length along the resistivity line.
[22] In this table we have not added the transition temperature data of the honeycomb sample etched for 112 s and 120 s because of possible inaccuracy in the T_c approximations for those samples. Although in Fig. 3 we have added the transition temperature data of the samples etched for 112 s, but it is calculated by extrapolation of the R-T curve for that sample and hence there is a possibility of an inaccurate approximation in obtaining the T_c value.
[23] S. Maekawa and H. Fukuyama, J. Phys. Soc. Jpn. **51**, 1380 (1982).
[24] The coherence length is determined by fitting the equation $H_c = \Phi_0/2\pi\xi^2(T)$ to the H_c vs T data, described in M. Tinkham, *Introduction to Superconductivity*, 2nd ed. (McGraw-Hill, New York, 1996), Chap. 4.
[25] W. L. McMillan, Phys. Rev. **167**, 331 (1968).
[26] *Handbook of Chemistry and Physics*, 73rd ed. (CRC Press, 1992).
[27] L. G. Aslamozov and A. I. Larkins, Phys. Lett. **26A**, 238 (1968).
[28] R. Ivens, R. Wernhardt, M. Rosenberg, S. Losch, and S. Sack, Supercond. Sci. Technol. **5**, 16 (1992).
[29] P. Clippe, C. Laurent, S. K. Patapis, and M. Ausloos, Phys. Rev. B **42**, 8611 (1990).