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This paper reports an experimental study of quench-condensed disordered ultra-thin films of Bi, where localization effects and superconductivity compete. Experiments are done with bare substrates and/or underlayers of solid Xe, Ge and Sb. The deposition temperature is also varied. We have observed absence of superconductivity in low dielectric constant substrates even though the sheet resistance is varied over 5 orders of magnitude. RHEED studies indicate that quantum size effects are important in these systems. Apart from stabilizing the amorphous phase in Bi, the Ge underlayer is found to nucleate superconductivity when the Bi was quench-condensed at 15 K. The macroscopic properties of the film are dependent both on the underlayer as well as the deposition temperature.

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DISORDERED thin films are systems where two opposing phenomena, viz. superconductivity and localization compete and lead to very interesting fundamental physics. This is because in two dimensions, a superconducting transition is barely possible since it is a manifestation of long-range coherence between electron pair states, and preventing this coherence is localization which occurs even for weak disorder. This is in contrast to the situation in three dimensions, where a critical degree of disorder is required for localization. Despite many studies of the phenomenon, a comprehensive understanding of the interplay between localization and superconductivity has been elusive<sup>1,2</sup>. The phenomenon is also of relevance in the context of high temperature superconductors, where the layered structure has been thought to imply two-dimensionality. Microstructural perturbations, in the form of stacking faults, cation anti-site disorder, etc. are unavoidable in these materials. The high- $T_c$  compounds are unfortunately not model systems for the investigation of this phenomenon, since they are only ternary and higher order compounds, making their synthesis a complicated materials issue. Also, in several of these materials the uncontrollable and temporally varying nature of oxygen doping of an insulating magnetic parent compound also affects their transition temperature.

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Many experimental results in this field have come from studies on thin and ultra-thin ( $\sim 50$  Å) films of Bi, Pb, Al, Sn, Ga, etc. deposited on to substrates held at low temperatures ( $\sim 20$  K or less)<sup>3-7</sup>. Superconductivity has been observed in such films in the temperature range 1–10 K. There has also been some evidence of a superconductor–insulator transition occurring at a certain value of (normal state) sheet resistance, independent of the material and microstructure of the film<sup>8</sup>. The choice of thin films is quite natural, since in two-dimensional systems the effect of microscopic disorder is more pronounced on the thermodynamic properties compared to three-dimensional systems. Though disorder is inherently difficult to quantify, there can be little doubt that several experimental parameters like

roughness of the substrate, presence of an underlayer (if any), temperature of condensation, interstitials, vacancies, etc. affect the microscopic disorder.

Some of these materials exhibit an enhancement of the transition temperature in their disordered thin film form. Notable examples are Bi, Ga and Al. Several arguments have been advanced in order to explain the physical origin of this enhancement. Anderson's<sup>9</sup> theorem of pairing time reversed states can only be used to explain the fact that these systems exhibit superconductivity, not the enhanced transition temperatures. Other explanations such as an increase in the density of states near the Fermi level due to the disordered nature of the material can be used to explain the enhancement of the transition temperature in semi-metals such as Bi (ref. 10). However, such an explanation is unable to account for the increase in the transition temperature of granular aluminum-aluminum oxide films, upon further exposure to oxygen. Yet another explanation invokes an enhancement in the phonon density of states due to softening of the phonon spectra, caused by an increase in the surface-to-volume ratio of the films<sup>11-14</sup>.

As will be pointed out here, these explanations turn out to be inadequate. Firstly, they do not account for effects of microstructure of the films, since studies of microstructure and properties have not been done simultaneously in situ in a clean UHV type environment. Secondly, there have been certain differences in the reported transition temperatures of these films, depending on the deposition conditions, and the presence of an underlayer (such as Ge or Sb which was thought to improve the wetting properties of the film). It is also necessary to note that such films are composed of small clusters. Anderson<sup>9</sup> was the first to address the problem of superconductivity in such small samples. If the electronic eigenspectrum of the sample becomes discrete, with a level spacing  $d = 1/N(e_F) P 1/vol.$ , superconductivity would no longer be possible when  $d$  becomes larger than the bulk gap  $\Delta$ . Giaver and Zeller studied tunneling in granular Sn films containing metallic islands in an insulating substrate<sup>15,16</sup>. Although a superconducting energy gap was found for grains right down to 25 Å radii, these studies were unable to prove that smaller particles are always normal. In this size region, the bulk theory of superconductivity loses its meaning. It may be incorrect to regard the particles as metallic because the energy level spacing is large compared to  $kT$  and because there are very few electrons at the Fermi surface. The question of the lower size limit for superconductivity is, therefore, strongly correlated with the definition of superconductivity itself<sup>17</sup>.

These remarks clearly demonstrate why the study of superconductivity near its lower size limit is of fundamental importance. The conventional BCS bulk approach is not directly applicable due to the finite number of particles involved. Several aspects of the theory need revision, in the light of level discreteness. First experiments in this direction were done by Strongin et al.<sup>5</sup> and a theory was developed by Mühlischlegel et al.<sup>18</sup> who calculated the specific heat and susceptibility of small superconducting grains.

The configuration studied in this work, namely films on top of inert gas substrates, has never been investigated. The ideal substrate for studying the insulator-superconductor transition is vacuum. The experimental impossibility of suspending atoms in vacuum and conducting transport measurements on them necessitates the use of a solid substrate. The role played by the substrate in studies conducted thus far remains unclear<sup>19</sup>, although it is generally acknowledged that the character of disorder which is of importance in determining the nature of the

transition is primarily microstructural in origin. This is because little or no knowledge exists about the surface structure of the substrates that have been in use thus far. They have been considered to be 'atomically smooth'. It is to be noted, however, that no surface can match a low index plane of a single crystal for atomic level smoothness. The nature of the surface is of paramount importance in establishing microstructural features. The deposition of a layer of presumably amorphous Ge or Sb has also been claimed to improve the smoothness of these substrate surfaces, although no structural investigations exist to confirm this. The reason for using Xe is because of its low dielectric constant than Ge, it is expected to play a less significant role in electronic conduction. The motivation for using Xe arises from the fact that it condenses at a relatively high temperature (161 K) and it should be possible to deposit a low latent heat of vaporization superconductor on this layer of Xe without disordering it. Amongst the conventional superconductors, Bi has a low latent heat of vaporization. This energy is important since it is dissipated at the substrate surface as film atoms strike it. The dissipation may take two forms, one of which is to use up the energy in diffusing over the surface, the other being to cause vibrations of the substrate atoms, which eventually die out. It is important to minimize the surface diffusion distances in order to grow uniform films, since enhanced surface diffusion can promote clustering and hence granularity.

In this work we report a systematic study of the effect of substrate dielectric constant, underlayers of Xe, Sb, Ge and deposition temperatures on transport properties of quench condensed Bi films. We find that the dielectric constant of the substrate/underlayer is an important parameter that governs the properties of the film, and may even help in inducing superconductivity. We also find that for a given underlayer, the temperature of deposition influences the onset of superconductivity. We attribute this to differences in the microstructure of the films grown at different temperatures. We believe these results have important implications for understanding the interplay between superconductivity and localization and the mechanism of superconductivity in disordered two-dimensional systems.

## Experiment

### Apparatus

The experiments were done in a UHV cryostat custom designed for in situ experiments. The cryostat is pumped by a turbomolecular pump backed by an oil-free diaphragm pump. The system is equipped with a Residual Gas Analyser to check for any contamination and cold leaks from the cryostat. A completely hydrocarbon-free vacuum  $\sim 5 \times 10^{-10}$  Torr can be attained. The cryostat is also equipped with a reflection high energy electron diffraction (RHEED) gun of 10 kV, so that the RHEED beam is incident upon the sample at a glancing angle of 1–2°. This minimizes the momentum transfer to the film, ensuring that the energy transfer is less than the latent heat of vaporization. The RHEED beam current is kept at the lowest possible level in order to obtain a diffraction pattern, which is acquired by a CCD camera and a frame grabber interfaced to a PC. Nevertheless, problems of beam deflection and instability due to surface charging effects could not be avoided. RHEED intensity oscillations were monitored as a function of deposition time.

The substrate holder is a copper cold finger whose temperature can be maintained down to 1.6 K by pumping on the liquid helium bath directly. The material (Bi) was evaporated from a Knudsen-cell, with a pyrolytic boron nitride crucible of the type used in Molecular Beam Epitaxy (MBE). The temperature of the cell was kept at 675°C and was stabilized correct to 1 degree. Successive liquid helium and nitrogen-cooled jackets surround the substrate, minimizing the heat load and providing cryo-pumping. The metal flux from the evaporation cell reaches the substrate through a small, carefully aligned opening on the nitrogen shield, guarded by a shutter. The flux reaching the substrate is about 5–6 Å/min and the thickness of the film is increased by small amounts (less than an Å) near the onset of conductivity, by opening the shutter for a few seconds.

### Xe condensation

In the experiment involving the Xe underlayer, ultra-pure Xe gas was let into the system at a pressure of  $\sim 1 \times 10^{-6}$  Torr through a precision leak-valve. At this partial pressure, a clean surface maintained at liquid helium temperature adsorbs about a monolayer of Xe per second. The exposure was timed to allow about 30 Å of Xe to get condensed. In order to ensure that this thickness of xenon has indeed condensed on the surface, an experiment involving condensation of Xe on single crystal sapphire at 77 K was done. This resulted in RHEED intensity oscillations (Figure 1). Although the origin of these oscillations is a matter of debate<sup>20–23</sup>, we

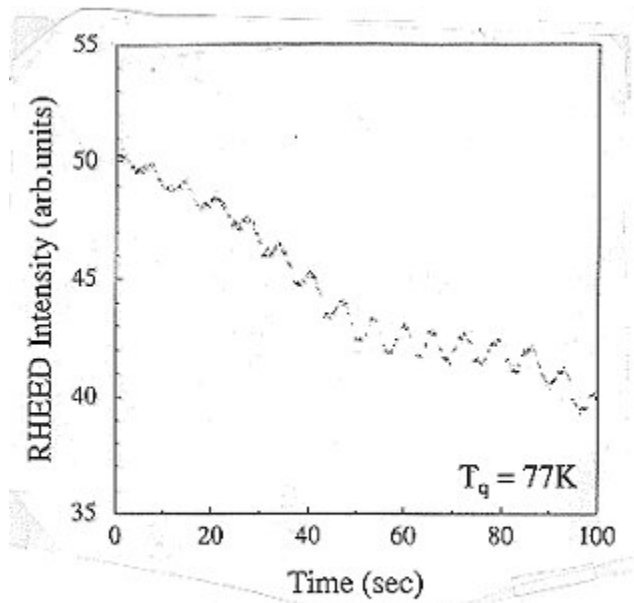
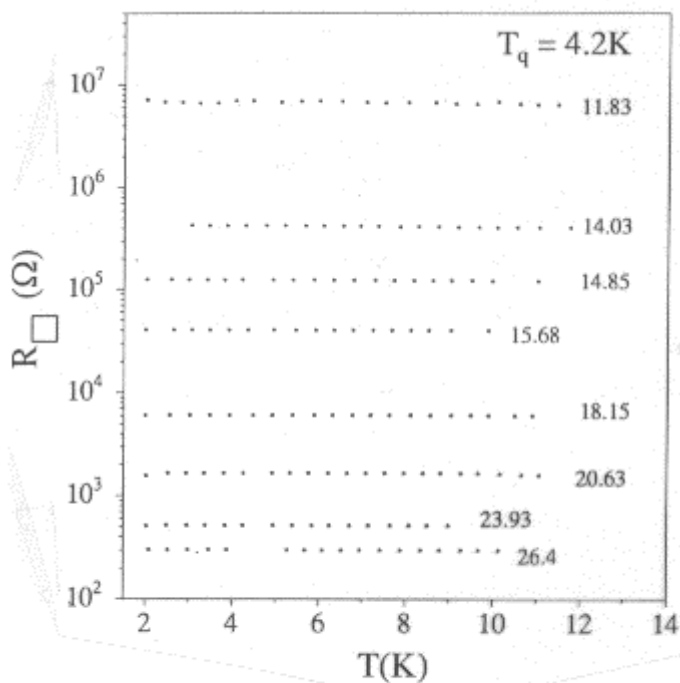


Figure 1. Intensity oscillations of RHEED spot during Xe condensation on (0001) sapphire substrate.



**Figure 2.** Evolution of resistivity vs temperature for Bi films on a quartz substrate ( $T_q$  – Quench-condensation temperature). The numbers on the right give the nominal film thickness in Å.

find that their time period is not inconsistent with an interpretation of completion of a monolayer and smoothening of the surface. If we assume one of these oscillations to indicate the completion of one layer, we can be sure that at lower temperatures of 4 K where desorption is much lower, at least 20 layers of Xe would have condensed on the substrate in the time period corresponding to 20 RHEED oscillations at 77 K. This would completely isolate the deposited Bi film from the substrate underneath, effectively floating the Bi film on a layer of Xe. Similar techniques have been used to isolate layers of metals from semiconductor surfaces by using buffer layers of Xe<sup>24</sup>.

There are several characteristic energies that are involved in the problem. To a first approximation, the adsorption energy  $E$  determines the temperature at which adsorption occurs. The value of  $E$  for Xe is the highest amongst all inert gases, being 1838 K on exfoliated graphite. The adsorbate–adsorbate interaction energy parameter  $V$  determines the temperature at which ordering in an adsorbed layer occurs. For all of the inert gases, a two-dimensional condensed phase (either a liquid or a solid) forms roughly at a temperature of  $0.5 V$  ( $V$  for Xe is 226 K). This small value of  $D$  allows condensed phases in which the adsorbed molecules are incommensurate with the substrate. The smaller value of  $D$  relative to  $E$  results because the adsorbate–substrate distance is smaller than the inter-atomic distance on the substrate. Thus the Bi atoms are far enough above the surface to only weakly sense the variations in the substrate plane electron density. This is a matter of considerable importance when measuring the properties of extremely thin overlayers, such as the ones we investigate.

Contacts and measurement

The substrate with pre-deposited platinum contact pads ( $\sim 50 \text{ \AA}$  thick) (and Ge or Sb underlayer  $\sim 10 \text{ \AA}$  thick, if used) was mounted on the cold finger. 46 SWG copper wires heat sunk to the cold finger and walls of the sample insert, were bonded to the Pt contacts using room temperature cured silver filled epoxy, which can withstand thermal cycling and has no measurable outgassing rate at room temperature and below.

The four-probe d.c. electrical resistance was measured by passing 5–50 nA of current supplied by a current source and recording the voltage developed through a nanovoltmeter. The measuring current to be used was determined after I–V characteristics were acquired over a couple of decades, and ascertaining that these are linear at each increment in thickness. In some cases, a.c. lock-in technique was also used.

## Results

Figure 2 shows the evolution of  $R_{\square}$  vs  $T$  of Bi films deposited on a bare quartz substrate held at 4.2 K. We find no onset of superconductivity in the range of thickness and temperature probed. The order of thickness at which a measurable conductance appears is about 10–15  $\text{\AA}$ . A qualitatively similar  $R_{\square}$  vs  $T$  is observed with a bare crystalline sapphire (0001) substrate also. The behaviour of the resistance, which shows negligible dependence on the temperature is intriguing and we now discuss this aspect in a qualitative manner.

RHEED studies indicate that these thin Bi films are either nanocrystalline or almost amorphous. We find it difficult to distinguish between these two regimes of microstructure at such low temperatures, on poorly conducting films, where charging effects preclude the possibility of an unambiguous distinction. Based on the Scherer formula for the peak broadening, we estimate that the films are composed of clusters that vary in size from 25 to 100  $\text{\AA}$ . Landau et al.<sup>25</sup> have modelled the structure of strongly disordered films, in the zero energy approximation of condensing atoms. We find that this type of a model is quite satisfactory to describe the microstructure of the Bi films, since Bi has a relatively low latent heat of vaporization. Inclusion of this energy does not yield qualitatively different results from those discussed here. The hard sphere model is used in these studies, and it is assumed that each new atom travelling with random coordinates in the direction of the substrate is trapped upon first contact with any of the previously deposited atoms and can then move by maintaining contact with only this first atom. Such motion occurs up to the nearest point where the new atom makes contact with at least three other atoms already on the substrate. Trapping of the atom upon first contact and the absence of film rearrangement with increasing film thickness are rather natural assumptions at low energy of the incoming atoms. Such a model is a limiting case of the maximum disorder that is possible in a hard-sphere system. In actual conditions, the final binding energy released upon condensation of the atom can cause a rearrangement of an already existing structure. Such rearrangements will naturally serve to increase the density, although estimating the magnitude of this effect is very difficult. It would be natural to expect structural changes for such atoms even with a slight rise in temperature, and these manifest themselves as irreversible changes in the resistance of the films. These films, therefore, consist of clusters that vary in size from 25 to 100  $\text{\AA}$ , the atoms being loosely packed in these clusters, with no clearly defined lattice parameter. Although a hard-sphere model invites criticism of being unrealistic, we believe that it can serve as a reasonable first

approximation to the structure, and our RHEED results appear to be consistent with such an interpretation.

The effect of the substrate on the properties of the film may be expected to lessen if its polarizability and the possibility of the formation of interface states is minimized. In order to study this effect, we choose substrates of different dielectric constants. Single crystal sapphire (0001) orientation has a lower dielectric constant than amorphous quartz, with values reported in the literature being  $\sim 3$  and  $\sim 5$ , respectively<sup>26</sup>. The R vs T of a series of films grown on sapphire, under identical deposition conditions are shown in Figure 3. This set of data is qualitatively similar to that for quartz, with no signs of the onset of superconductivity. It is important to note that the onset of conductivity is at a higher thickness than on quartz.

Figure 4 shows the behaviour of resistance as a function of temperature when we raise the temperature beyond 20 K. We first notice a pronounced dip in the resistance which we believe is caused by annealing of short-range disorder. After this drop, the resistance rises sharply, an effect that we attribute to crystallization of Bi, and consequent reduction in the density of states. These observations are to be contrasted with the studies on the crystallization of Cu films reported by Cleveland<sup>27</sup>. In the case of semi metals such as Bi, microstructural disorder results in the development of a finite density of states near the Fermi level. Annealing of short-range disorder reduces the scattering and results in

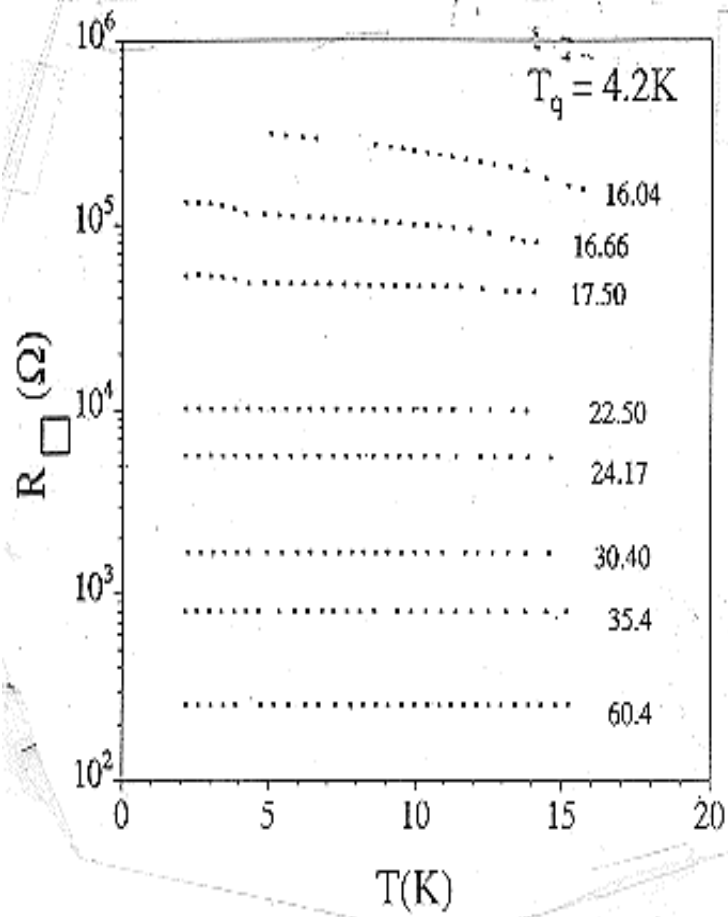
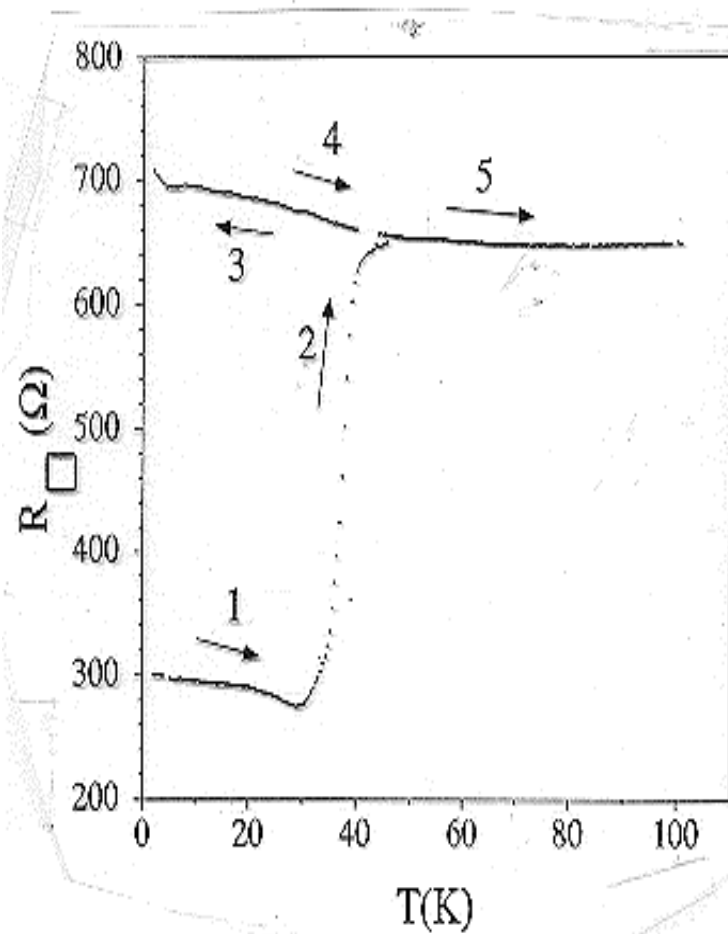


Figure 3. Evolution of resistivity vs temperature for Bi films on (0001) sapphire substrate.





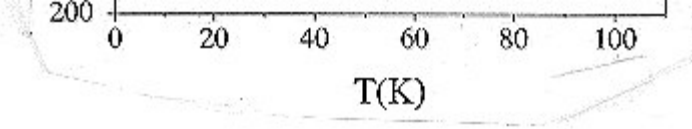


Figure 4. Annealing behaviour of the thickest Bi film of Figure 2.

a drop in resistance. Crystallization reduces the DOS and increases the resistance. Annealing and crystallization have identical effects in metals, although their effects in semi-metals can be quite different as these data demonstrate. These plots also establish that we are indeed dealing with highly metastable structures, as discussed earlier.

Results obtained by condensing Bi on a Xe underlayer are shown in Figure 5. Once again we notice an absence of any onset of superconductivity. The  $R-T$  traces show a very small but negative  $dR/dT$ . None of the traces shows an activated behaviour characteristic of insulating materials in this temperature range. Solid Xe has a dielectric constant of  $\sim 1.7$  (ref. 28), and the onset of conductivity is at a higher thickness than on sapphire. At this point, an observation that may be potentially important is in order. We note that the thinnest films are quite dirty, with a very small value of  $k_{FL}$ . However, for the thickest films we are well into the classical regime with  $k_{FL} \gg 1$ . The persistence of the temperature independence of the resistance, well into the classical regime is puzzling. This may be reconciled by considering Bi to be nanocrystalline so that it behaves as a semi-metal. We stress again that using only RHEED as a structural probe, we are unable to show with certainty that the films are truly amorphous or nanocrystalline.

It is also interesting to note that the Mooij correlation<sup>29</sup> does not appear to hold in these systems. The Mooij correlation, namely that in a large number of metallic conductors,  $dr/dT$  becomes negative when  $r$  is larger than a value ranging around  $80-180 \mu\Omega\text{cm}$  holds for over a hundred 'dirty' disordered systems. This almost 'universal' trend must have an explanation which is only weakly dependent on material properties, and we stress here that  $dr/dT > 0$  always in weak scattering theory. In our systems, we do not observe a negative  $dr/dT$  even in the strong scattering regime.

In the following, we discuss the results obtained on Bi films grown on a Ge underlayer, which has a dielectric constant of  $\sim 15$ . In these experiments, a  $10 \text{ \AA}$  thick Ge layer was pre-deposited on quartz at room temperature and the Bi films were grown on these underlayers. Such underlayers have been used earlier, and were thought to improve the wetting properties of the Bi films. The Bi films in these experiments were deposited at  $4.2 \text{ K}$  as well as  $15 \text{ K}$  (see Figure 6). Here, we find a small temperature dependence of the resistance, but it still does not exhibit activated behaviour or variable range hopping behaviour. We should also mention that the  $I-V$  curves for the thinnest films are nonlinear, as shown in Figure 7, with  $I \propto V^n$ , with  $n > 1$  even for the lowest measuring currents of  $5 \text{ nA}$  that we could use. The significance of this observation will be discussed later. The resistance of the Bi films deposited at  $15 \text{ K}$  drops sharply around  $4-5 \text{ K}$  to less than  $10\%$  of its value. We consider this to be a signature of the onset of superconductivity. Several points are worth mention and discussion. We note that the onset of conductivity is at a higher thickness in comparison to the films grown on bare quartz or sapphire, but at a lower thickness when compared to the films grown on Xe. The resistance is also very sensitive to the thickness for these films on

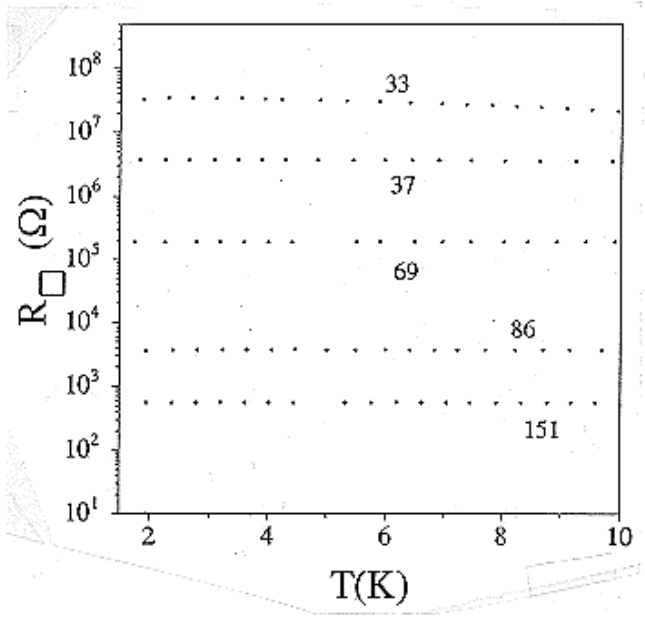


Figure 5. Evolution of resistivity vs temperature for Bi films deposited on physisorbed Xe underlayer. The Xe was adsorbed on a quartz substrate.

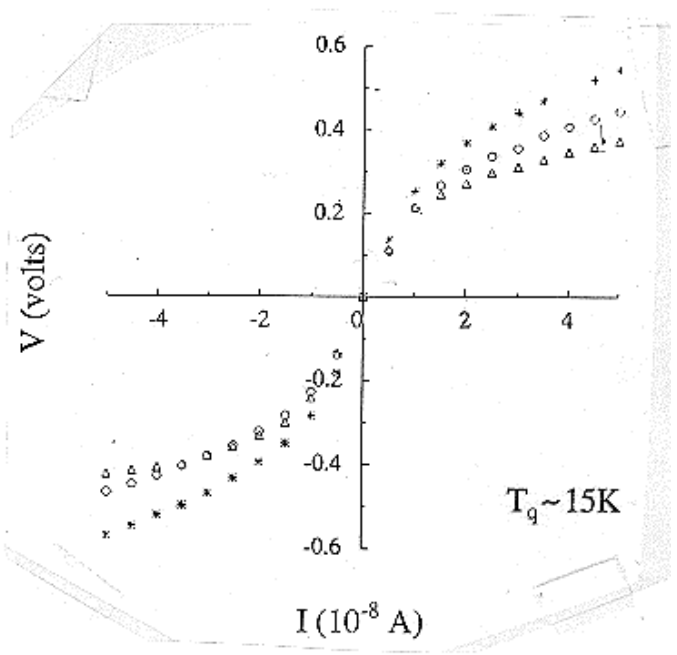
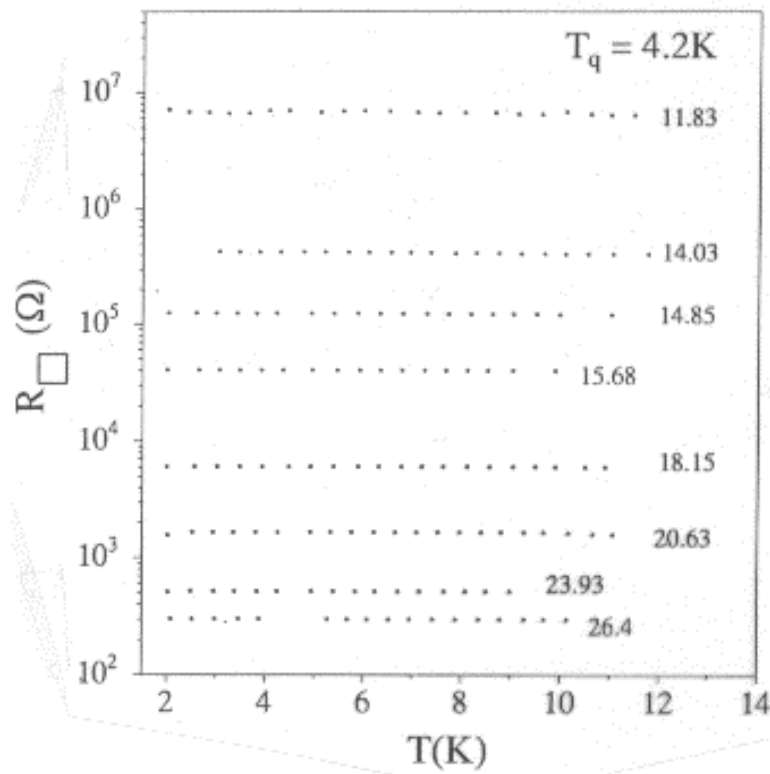


Figure 7. *I-V* characteristics for the thinnest Bi films of different thicknesses on Ge underlayer. The substrate was a quartz.



**Figure 2.** Evolution of resistivity vs temperature for Bi films on a quartz substrate ( $T_q$  – Quench-condensation temperature). The numbers on the right give the nominal film thickness in Å.

Ge, exhibiting a drop of over two orders of magnitude for an increase in thickness of only 3 Å, from 23 to 26 Å. For the 25 Å and thicker films, including the films that exhibit superconductivity, the normal state I–V characteristics were found to be linear. The dielectric constants of the Ge and Sb underlayers used in this work are around 15 (ref. 30).

These observations seem to suggest several possible scenarios. The Ge underlayer may actually stabilize the amorphous phase of Bi, thereby favouring the development of a finite density of states at the Fermi level. This explanation is reasonable, since Ge is amorphous, and the dangling bonds may improve the wetting properties of the Bi film, as postulated by earlier workers. The higher dielectric constant of the Ge film may enhance the screening of the Coulomb interaction between electrons, making the transition to the superconducting state easier. The enhanced screening effect, however, is not quite as straightforward as it appears to be, since the onset of conductivity is at a higher thickness on Ge. Screening, localization and interaction appear to be intimately connected in these disordered systems, with the Ge underlayer not playing a passive role as commonly believed. Evidence for this claim exists in the literature since Bi is reported to behave as a shallow donor in Ge (refs 31, 32).

Qualitatively similar results are obtained for Bi films grown on an underlayer of 10 Å Sb, predeposited at room temperature on amorphous quartz. Quench condensing the films at a lower temperature of 4 K did yield superconducting films, albeit with lower transition temperatures. This is quite understandable since the nature and extent of microstructural disorder are influenced by the temperature of deposition. Next, we briefly discuss the possible nature of conduction in the films deposited on Ge and Sb underlayers. Unlike the films deposited on bare quartz, sapphire or xenon substrates, the thicker films on Ge and Sb are superconducting, but the thinnest films show very weak or almost negligible temperature dependence of resistance. We believe that these films are amorphous, and that the nonlinear I–Vs are indicative of a mode of electron transport distinct from the mode of transport in films on bare substrates that show linear I–Vs.

## Discussion

Metal atoms condensed on to cryogenically cooled crystals should not be able to diffuse macroscopic distances, so considerably thinner continuous films can be produced by quench condensation. Yet, these films are never found to be atomically smooth, and have a large degree of quenched-in disorder. Recent simulations of quench-condensation, generally based on ballistic aggregation<sup>33–36</sup> give an indication of why such behaviour is to be expected when atomic diffusion is absent. In ballistic aggregation, atoms move towards a growing film and stick where they first hit, either on the substrate or on a neighbouring atom, forming a highly branched structure. Overhanging atoms shadow the space beneath them, leading to voids. Because of the unidirectional nature of the atomic beam, the interior of the film is effectively screened and maintains a constant density (the film is not fractal) as the film thickness increases. The actively growing surface of the film (layers in which new atoms may be added) has a thickness of 10 to 20 monolayers, and the voids in the film have length scales that vary from single-atom vacancies up to this interface thickness.

These comments on the evolution of thin film microstructure are important to gain a qualitative understanding of the transport in our quench-condensed films. Since we are dealing with two materials, the interface between them assumes an importance that has been neglected as our results demonstrate. Although there has been no mention of superconductivity in the Bi–Ge system itself, the fact that Bi acts as a shallow donor with an ionization energy of 12.75 meV in Ge is significant<sup>31,32</sup>. There is substantial evidence from a number of other two-

dimensional systems for the relevance of more traditional considerations relating to localization theory, in the disappearance of superconductivity in disordered systems. In this approach, the amplitude of the order parameter is suppressed by reduction of the screening of the Coulomb repulsion by disorder, and there is no universal resistance. An example of this is the work on homogeneous Mo–Ge films of various compositions reported earlier<sup>37</sup>. These films are amorphous, and their transition temperatures appear to be functions of sheet resistance consistent with considerations of localization and Coulomb repulsion<sup>38–40</sup>. Recent experimental work<sup>41</sup> on multilayer structures supports the view that the suppression of  $T_c$  is localization-related rather than surface-related. Our work seems to indicate that the onset of superconductivity is connected to the Bi–underlayer interface. Results of this nature have been reported quite recently in the literature<sup>42–44</sup>. Clearly, differences in the character of disorder are the source of variation in the properties of films grown under different conditions<sup>45,46</sup>. Further, structures of films in a sequence may change with successive depositions and temperature cycling. The existence of localized electronic states has significant consequences on electron transport in amorphous materials. Electron wave functions have a finite extension, of the order of the localization length  $a^{-1}$ , in contrast to the extended Bloch states in their crystalline counterparts. Electrons then move by one of two ways, namely elastic tunneling or inelastic hopping between localized states. Both depend on the overlap of the wave-functions of the two states involved, which itself depends on their spatial separation  $R$ :  $\exp(-2aR)$ . In addition, both depend on the probability of finding a state in the appropriate energy range. In the former case (tunneling), the tunneling rate is proportional to  $\Gamma$ , the energy width of the localized state (which again depends exponentially on the distance between the states), whereas in the latter case (hopping) it is equal to  $k_B T$ , the characteristic phonon energy. Since under most conditions  $k_B T \gg \Gamma$ , transport via tunneling can be neglected and hopping is the dominant conduction mechanism. At low temperatures, however, elastic tunneling may dominate the transport<sup>47–51</sup>. We believe that this discussion is a qualitative description of the physical process involved in the very weak temperature dependence of the resistance of the thinnest films on Ge. Corroborative evidence for this behaviour, over the temperature range from 5 to 16 K has been previously observed<sup>52,53</sup>, in the form of a nearly temperature-independent conductance, for Si barriers ranging in thickness from 60 to 150 Å. Due to the fact that their films were made from amorphous Si, using electron beam evaporated Nb as electrodes, and the deposition was done at room temperature, these authors could actually observe the cross-over to variable range hopping (VRH) as a function of temperature. Since we are dealing with quench-condensed thin films, which are highly metastable structures, we are unable to access the cross-over regime or the VRH regime before the film gets annealed/undergoes crystallization. Our studies thus appear to suggest that the amorphous Ge, apart from stabilizing the amorphous phase of the Bi also plays a role in the mechanism of conduction by providing localized states that form optimal conduction paths. Thus, it appears that merely increasing the dielectric constant by switching to substrates such as SrTiO<sub>3</sub> is unlikely to be of any benefit in influencing the onset of superconductivity. The electronic contribution to the dielectric constant appears to be extremely important. The nucleation of superconductivity in such systems clearly involves more phenomena than simple electron–phonon interactions. Whether Ge is a source of excitations that nucleate or enhance superconductivity in the Bi films is an issue that remains to be addressed by further experiments.

## Conclusion

We have observed an absence of superconductivity in quench-condensed thin films of Bi grown on several substrates of low dielectric constant. The normal state resistances of these films vary over 5 orders of magnitude as the thickness is increased. RHEED studies indicate that the films are nano-crystalline, and consist of clusters that are 25 to 100 Å in diameter. Thus, we are in a size regime where the single electron energy level spacings are comparable to the superconducting energy gap, and quantum size effects are very important. We believe that these films are semi-metallic, since their R vs T is almost temperature independent. When an underlayer of either Ge or Sb is used, we observe a transition to the superconducting state. This suggests that the dielectric constant of the underlayer is an important parameter in influencing the onset of superconductivity in these disordered systems. However, it is rather surprising that the threshold of thickness for a measurable conductivity to appear was nearly doubled in the presence of a Ge underlayer when compared to amorphous quartz or sapphire. This thickness, however, remains below the minimum thickness required for conducting films on solid Xe. The reason for this anomaly is not understood. This observation suggests that localization effects and superconductivity are intimately connected in these films. These experiments emphasize the fact that the establishment of phase coherence in disordered systems depends on many parameters and more detailed experiments are needed to have a complete understanding of the physics involved. It has been claimed from earlier experiments on onset of superconductivity in ultra-thin Sn films that the sheet resistance is the only relevant variable in determining the phase coherence<sup>54</sup>. In this work we have demonstrated that this is not the case for Bi films that are deposited on an underlayer of Ge.

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