Evidence for Superconductivity in Low-Temperature–Grown GaAs

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Magnetic-field-modulated microwave absorption and dc susceptibility measurements have detected evidence for superconductivity in As-rich GaAs layers grown by molecular-beam epitaxy at low temperatures (LT-GaAs). The transition temperature from the normal to the superconducting phase is 10 K. Electron microscopy of these layers found a new, As-rich layered structure in LT-GaAs that is most likely the origin of the superconductivity.

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The physics of nanostructures such as crystalline clusters is a rapidly developing field. One example of this is the superconductivity of metal clusters.[1] In Sn clusters the superconductive transition temperature was found to increase as cluster size decreases.[2] Recently superconductivity was found in a granular surface system of Bi clusters, although Bi does not show superconductivity in the bulk form.[3]

In this paper we report the discovery of a superconducting phase in a semiconductor host of As-rich GaAs grown at low temperature by molecular-beam epitaxy (LT-GaAs). LT-GaAs grown at about 200 °C and annealed at about 400–600 °C exhibits very high resistivity. Because of this property LT-GaAs is successfully used as an insulating buffer layer, practically eliminating backgating and sidegating of metal-semiconductor field-effect-transistor (MESFET) devices.[4] In addition, LT-GaAs is a very interesting material for gate isolation in metal-insulator-semiconductor FETs (MISFETs), and the short minority-carrier lifetime (in the fsec range) permits promising applications as the active layer in photodetectors and photoconductive switches.[5]

It is well established that LT-GaAs is strongly off stoichiometric, with up to 1.5% of extra As incorporated in these layers.[6,7] In as-grown layers, a large fraction of the excess As is incorporated in the form of anion antisite defects $\mathrm{As_{Ga}}$.[6] Hopping conduction between these antisite defects is observed so that as-grown LT-GaAs layers are generally quite conductive.[7–10] The as-grown layers exhibit a strong lattice expansion that scales with the amount of excess As.[6,11,12] The layers grow epitaxially up to a certain critical thickness that depends on the growth temperature and the layer stoichiometry, e.g., for growth at 200 °C and an As/Ga ratio in the layer of 1.01, at least 2 μm of material with high crystalline quality can be grown.[12] Upon annealing above 500 °C in the MBE chamber with As-stabilized surface the formation of a large number of As-rich precipitates is observed,[13,14] accompanied by the formation of a high-resistivity phase of the material. The properties of these precipitates and their influence on the properties of LT-GaAs is a hotly contested subject.[7,9,14] Our finding of evidence for a superconducting phase inside semi-insulating LT-GaAs will add a completely new dimension to this research area and will have implications far beyond the scope of this Letter.

Samples of LT-GaAs were investigated by magnetic-field-modulated microwave absorption (FMMA) in an electron paramagnetic resonance (EPR) experiment. A Bruker EPR ER-200D spectrometer was used working near 9.4 GHz and employing 100-kHz field-modulation amplitudes from 5 mG to 28 G. The FMMA signal thus measured was the field derivative of the microwave absorption. A pair of externally fed Helmholtz coils allowed negative magnetic-field offset for sweeps around zero field. Temperature variation from 4 to 300 K was obtained with a He gas flow cryostat. A thermocouple mounted 10 mm below the sample allowed us to determine the sample temperature with an accuracy of ± 0.5 K. Additional static magnetic-susceptibility measurements were made using a SQUID VTS-805 magnetometer.

Samples grown by MBE in various laboratories on semi-insulating GaAs substrates were investigated. The growth temperatures of the LT layers ranged from 180 to 210 °C. Some of the samples were as-grown, others were annealed *in situ* at 550–600 °C during subsequent overgrowth of a GaAs layer. In all cases the LT-GaAs layers were 1–2 μm thick. All samples investigated were analyzed by particle-induced x-ray analysis[7] and found to contain between 1% and 1.5% of extra As.

Most of the investigated LT-GaAs layers showed at low temperatures a characteristic FMMA signal near zero field. A typical example is shown in Fig. 1 where the FMMA spectra were recorded at different temperatures. At low temperatures a minimum in absorption (integrated FMMA signal) was observed at $H=0$ with a 15–20-G peak-to-peak width. A qualitative change of the character of the absorption took place above 10 K. Above 11.5 K the signal disappeared completely. This behavior clearly indicates a phase transition in this temperature range. The FMMA signal was independent of the orientation of the sample with respect to the external magnetic field.

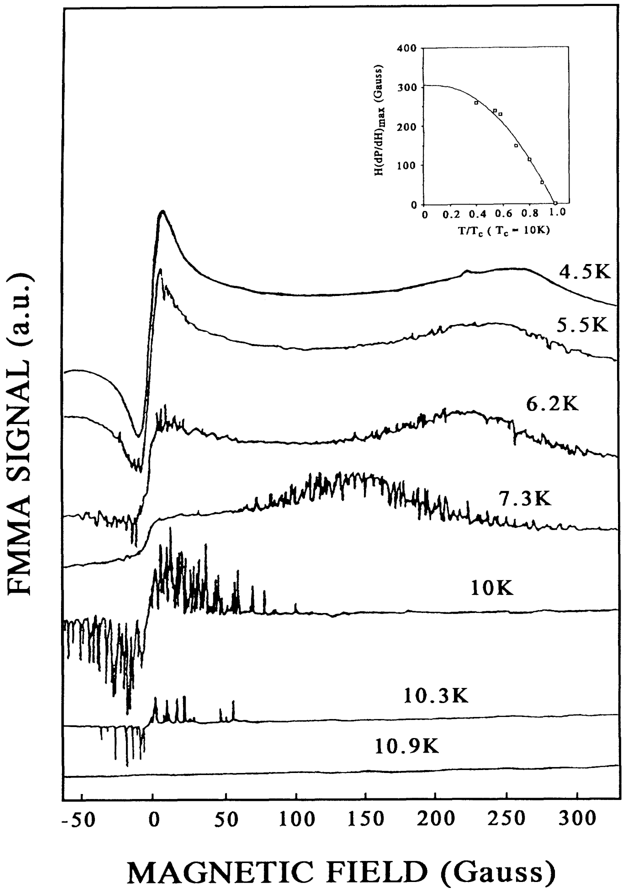

FIG. 1. Typical temperature dependence of field-modulated microwave-absorption (FMMA) signal in LT-GaAs. The base line for each temperature is offset to show the temperature effect. The incident microwave power is 20 mW, field-modulation amplitude is 5 G, and amplifier gain is 4×10^3 (maximum gain for this microwave power is 4×10^6). Inset: The temperature dependence of the position of the high-field peak, with a fit given in the text.

Another interesting feature of the spectra shown in Fig. 1 is a local maximum in FMMA amplitude observed at $T=4.5$ K near 260 G. This maximum was found in all samples showing the characteristic absorption near zero field . Reversing the field direction shows a corresponding minimum symmetrical to that maximum at negative field. Figure 1 shows that the position of this peak is strongly temperature dependent near the transition temperature. It approaches zero magnetic field at the critical temperature, which is shown in the inset, Fig. 1.

A further characteristic observation is the increase of noise as the temperature approaches the transition temperature. The noise level of the instrument for the gain setting used for all these spectra is displayed in the 10.9-K trace. For temperatures between 7.3 and 10 K, strong positive and negative noise spikes are observed near the FMMA maximum for positive and negative fields, respectively. The amplitude of the spikes increases near the critical temperature, but they disappear completely above 11 K.

The FMMA signal depends strongly on the field modulation amplitude. The field dependence of the signal shows an open hysteresis loop with a change of sign accompanying each field-sweep reversal; see Fig. 2. With increasing modulation amplitude the loop closes. The spectra shown in Fig. 2 illustrate two examples, for 10-mG and 1-G modulation amplitude. The signal amplitude measured at about 8 G is linear with modulation field for variation from 5 mG up to 16 G.

The FMMA signal observed in LT-GaAs is very similar to the characteristic microwave absorption found in high-T_c superconductors. Soon after the discovery of high-T_c superconductors[15] many reports of the microwave absorption of these materials were published.[16-21] In a dc magnetic field the microwave absorption shows a minimum at zero magnetic field and saturates at higher fields. At temperatures well below T_c, the microwave-absorption signal near zero field typical for granular superconductors has been associated with damped fluxon motion,[20] critical-state current,[18] and fluxon-induced[19] decoupling of Josephson junctions at the surface of the superconductor.

The other characteristic feature of high-T_c supercon-

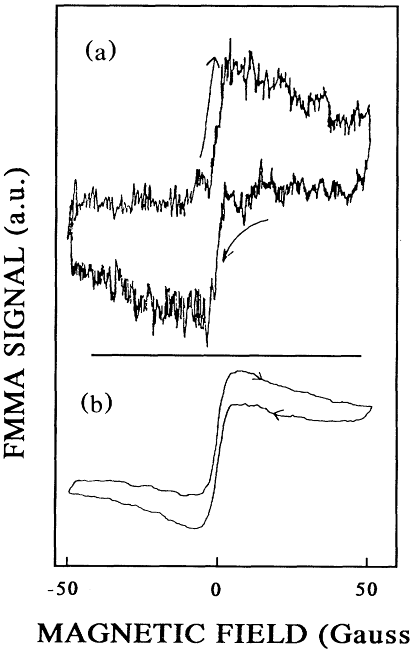

FIG. 2. Hysteresis in field-modulated microwave absorption measured with (a) 10-mG and (b) 1-G modulation amplitude. The amplifier gain is adjusted to compensate for the increase in signal magnitude. Sample temperature is 5 K and the incident microwave power is 20 mW.

ductors is the microwave-absorption hysteresis such as shown in Fig. 2. The exposure of a granular superconductor sample to a magnetic field decouples the grains so that the magnetic susceptibility of the sample is that of isolated superconductive grains rather than of coupled clusters of grains. When the magnetic field is removed, flux remains trapped in intergranular Josephson junctions[18,21] so that a microwave-absorption hysteresis can be observed upon reversing the field-sweep direction. This near-zero-field absorption hysteresis is uniquely observed only in superconducting material and is a further evidence of the presence of a superconductive phase in LT-GaAs.

In addition to the FMMA signal around zero field, another signal with maximum at 260 G at $T=4.5$ K is observed in all investigated samples that showed the near-zero-field absorption. This peak always showed a strong temperature dependence; see Fig. 1. Its presence indicates the onset of another field-induced microwave-absorption process. The temperature dependence of this peak can be fitted well with $H_p(T)=H_p(0)[1-(T/T_c)^2]$, with $H_p(0)=310$ G. This temperature dependence suggests that $H_p(T)$ might be related to the lower critical field H_{c1} so that this new microwave absorption might be due to damping of fluxons penetrating into the bulk of individual superconductive grains. The onset of this signal suggests $H_{c1}(0)=200$ G.

The increased FMMA fluctuations when the temperature approaches the critical temperature (Fig. 1) indicate a sharp, supposedly superconducting phase transition. However, the temperature range in which these fluctuations are observed is rather wide and difficult to reconcile with the notion that these might be the critical fluctuations characteristic of the phase transition from a superconductive to normal state.[22]

Although the origin of these field-modulated microwave-absorption signals is not yet fully understood, there is no doubt that these characteristic low-field signals are uniquely caused by the presence of superconductivity. Most of the investigated LT-GaAs samples displayed some FMMA characteristic of a superconductive state; its magnitude was found to differ by up to 2 orders of magnitude.

To independently confirm the existence of superconductivity in these samples, a Meissner-effect experiment was performed. The static magnetic susceptibility of the samples was measured from 40 to 5 K with 500 G of applied magnetic field. Figure 3 shows representative results. The negative susceptibility background is due to the GaAs substrate. The positive increase from 40 to 10 K is linear in $1/T$ with a slope of 2.3×10^{-7}/K. It is indicative of residual paramagnetic impurities in the sample. At 10 K, there is a break in the slope due to an increased diamagnetic contribution to the signal. This effect is further evidence of the existence of superconductivity within the sample with a T_c close to 10 K. A lower limit for the volume of the superconducting material is estimated by subtracting the measured value of the susceptibility at the lowest temperature of 5 K from the $(1/T)$-extrapolated value at this temperature. This difference divided by $-1/4\pi$ gives the volume of the superconducting material of at least 1.3×10^{-8} cm^3 (see inset in Fig. 3), which corresponds approximately to 0.01% of the volume of that LT-MBE layer.

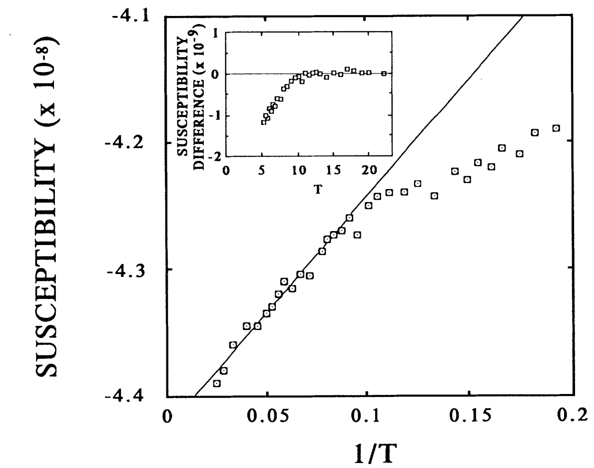

FIG. 3. Static magnetic susceptibility (cm^3/cm^3) of a sample with strong FMMA as a function of reciprocal temperature. The applied magnetic field is 500 G. The straight line fits the paramagnetic contribution above 10 K. Inset: The difference between the measured susceptibility and the paramagnetic contribution.

The question arises as to what kind of phase may be responsible for the observed superconductivity. It seems to be connected with the excess of As in LT-GaAs layers, with larger FMMA signal observable for larger As/Ga flux ratio during crystal growth. However, no superconductivity can be found down to temperatures of 15 mK in As of rhombohedral structure (usually referred to as hexagonal As) at atmospheric pressure.[23] Under hydrostatic pressure of about 24 GPa, As in the rhombohedral phase becomes a superconductor with a critical temperature of 2.7 K.[24] However, it seems unlikely that an extrapolated pressure of the order of 100 GPa (for a transition temperature of $T_c=10$ K) may exist in LT-GaAs layers. More importantly, in this case strain variations, including annealing that was found to remove the considerable strain in as-grown LT-GaAs,[7,11,12] would result in different transition temperatures. On the other hand, the recent finding[3] that Bi surface clusters with rhombohedral crystal structure show superconductivity with T_c up to 5 K, in contrast to bulk Bi, demonstrates that As-rich clusters may still be responsible for the superconducting state.

A wide variety of LT-GaAs samples of various origin were investigated by transmission electron microscopy (TEM), with special attention to differences between those samples which exhibit strong superconducting FMMA and those which show no or only a very weak effect. In samples that showed a strong superconducting response, evidence for $\mathrm{As_{Ga}}$ antisite defects in $\{111\}$ and $\{112\}$ twin planes was found.[25] The qualitative correlation of the occurrence of these defects with the magnitude of the FMMA superconducting response leads us to propose that an arrangement of antisite defects in twin planes might be the origin of the superconductivity in LT-GaAs.

In conclusion, field-modulated microwave absorption and Meissner effect show clear evidence for the existence of a hitherto unknown, superconducting structure in As-rich GaAs grown by MBE at low temperature. Transmission electron microscopy suggests that the superconductivity might be due to a new, As-rich structure in LT-GaAs. This discovery was only possible with the help of modulated microwave absorption. This technique was found to be extremely sensitive: An extrapolation shows that FMMA allows us to unambiguously detect a superconducting phase of only 10^{-6} of a nonmetallic matrix. Therefore this technique will be ideally suited for detecting other superconducting clusters or diluted phases, as pointed out earlier.[18]

The discovery of superconductivity in LT-GaAs has important practical consequences in addition to its scientific relevance. It can be expected that similar anion-rich low-temperature-grown layers of semiconductor compounds and alloys will exhibit superconducting transition temperatures above the 10 K found here for LT-GaAs. It is now possible, for the first time, to think of combining on the same chip insulating, semiconducting, and superconducting devices, based on epitaxially grown layers. This might result in completely new directions of device technology, including epitaxial superconducting interconnects, junctions, and switches.

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