^{4}He-Induced Damage in Superconducting Nb-Ge Films

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Defects introduced into superconducting Nb-Ge films by 2-MeV ^{4}He particles produce a T_c-resistance-ratio correlation similar to that for as-grown films and a T_c-lattice-parameter correlation resembling both film and bulk behavior. It is suggested that simple antistructure defects in a perfect lattice are not primarily responsible for lowering T_c for the case of ^{4}He damage in the sputtered films.

The discovery[1-4] that thin films of Nb-Ge can have superconducting onset temperatures of ~22–23 K has stimulated considerable interest as to their nature. It has been suggested that the high T_c's are due to the formation of the stoichiometric $A15$ phase, Nb_3Ge. However Testardi *et al.*[4] investigated a wide variety of sputter-deposited films with onset temperatures varying from 4 to 23 K and found that, although composition is important, it is not the most crucial factor responsible for the high T_c's in the sputtered films. From Rutherford backscattering, x-ray, and resistivity measurements, it was concluded that a key factor which determined whether the T_c was low or high was the presence or absence of microscopic defects. We present below the results of ^{4}He-damage studies of superconducting Nb-Ge films where defects can be introduced in the films in a controllable fashion at constant chemical composition. We find, in particular, that the defects produced by the ^{4}He particles produce a T_c-resistance-ratio correlation similar to that found in as-grown films and bulk and a T_c-lattice-parameter correlation which resembles both the film and the bulk behavior. These results, therefore, may carry a clue to the hidden defects which are detrimental for superconductivity in Nb-Ge.

Recently Meyer, Mann, and Phrilingos[5] have demonstrated that the T_c's of superconducting $A15$ Nb_3Sn films can be reduced from an initial T_c of 17.8 to 2.0 K by implantation of Ar ions to a dose of 10^{16} cm^{-2}. This decrease was attributed to damage effects and probable change in long-range order. A large depression of T_c with neutron irradiation has been reported by Bett.[6] Sweedler, Schweitzer, and Webb[7] have damaged a series of the $A15$ compounds with high-energy neutrons and shown that the fractional changes in the respective T_c's, versus neutron dose, lie on a universal curve. There is a threshold at ~10^{18} neutrons/cm^2 before significant depression in T_c occurs; after a dose of 5×10^{19} neutrons/cm^2 Nb_3Sn, for example, experiences a decrease in T_c from 18.1 to 2.8 K. It was deduced from the sensitivity to damage and from x-ray and neutron diffraction measurements that the decrease in T_c is primarily due to disordering of the lattice with the interchange of A and B sites in the A_3B lattice, i.e., the formation of antistructure defects.

The sputter-deposited films were prepared as described previously[4] and were chosen to have Nb/Ge composition ratios close to 3/1 with thicknesses ~3000 Å. The samples were bombarded with 2-MeV ^{4}He at a particle density of 10^{13} cm^{-2} sec^{-1} and maintained at a temperature of no greater than 50°C above room temperature. Pressures during bombardment were ~10^{-6} Torr. Resistances of the samples before and after bombardment were determined by use of a standard four-probe ac resistance measurement with pressure contacts. Resistivities at 300 K before bombardment were ~70–100 $\mu\Omega$ cm.[4] Temperatures were measured to an accuracy of ±0.2 K with calibrated germanium resistors and/or a silicon diode. X-ray diffraction data were obtained by use of a wide-film Debye camera and Cu $K\alpha$ radiation which allows the detection of diffracting planes having preferred orientation at considerable angles to the plane of the sample substrate.[4]

Figure 1 shows T_c versus ^{4}He dose for a set of films of high initial T_c (22 K) before bombardment and one film with a low initial T_c of 9 K. Consider the upper curve of the high-T_c films —the dashed lines are meant to guide the eye. There is a plateau region for doses $\lesssim 5\times10^{15}$ where the T_c's are not significantly changed. This dose is approximately equivalent to the neutron threshold dose of 10^{18} cm^{-2} of Sweedler and co-workers[7] as we now show. 2-MeV ^{4}He particles will lose ~100 keV in traversing the 3000-Å Nb-Ge films and penetrate some 5 μm into the sapphire substrates. This 100-keV energy loss (≡30 eV/Å) in the films is almost entirely due to

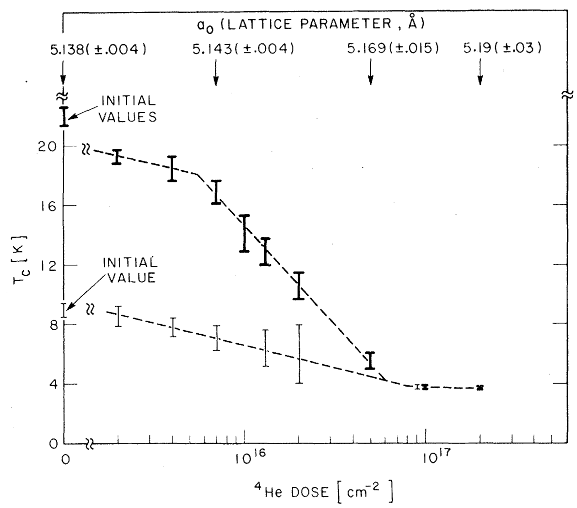

FIG. 1. T_c versus ^{4}He dose for films with starting values of 22 and 9 K; T_c's are onset and completion temperature (± 0.2 K) of resistive transition. Lattice constants of the 22-K films as a function of dose are also shown.

electronic excitations. Energy lost to nuclear recoils can be calculated from Bohr[8]; assuming a maximum energy transfer of 0.32 MeV (for head-on collisions) and a minimum of 25 eV (for an impact parameter of 0.03 Å), the energy loss to nuclear recoils will be ~0.05 eV/Å. This is the energy-loss process that will produce damage in the films. The approximate damage equivalence between fast neutrons and 2-MeV ^{4}He can be calculated from Robinson[9] who gives the specific damage energy of 1–2-MeV neutrons as ~10^{19} eV cm^2. Equating energy deposition with damage, 10^{18} neutrons/cm^2 will be equivalent to 10^{15} ^{4}He/cm^2. This is an oversimplification as the morphology of the damage will probably differ because of the different recoil spectra. There have been no detailed studies of radiation-induced defects in *A*15 materials; however, they are expected to run the gamut of isolated point defects to large interstitial or vacancy clusters.[10]

The damage curve for the high-T_c films shows a plateau region, a region (5×10^{15}–5×10^{16} cm^{-2}) where T_c rapidly degrades, according to $\Delta T_c \propto \ln(\text{dose})$, and a saturation region ($>10^{17}$ cm^{-2}) where $T_c \sim 3.5$ K does not degrade with ^{4}He bombardment. An interesting feature is that the widths of the superconducting transitions decrease markedly once the saturation region has been attained, indicating that a homogeneous state has been achieved. The sensitivity of Nb-Ge thin films to damage is illustrated by comparing the present T_c measurements for doses of 5×10^{16} cm^{-2} with corresponding bombardment of 3000-Å Nb films. The sputter-deposited Nb films had initial T_c's of 9.3 K with width of 0.1 K and after a 5×10^{16}-cm^{-2} ^{4}He bombardment the T_c had only decreased to 9.1 K with the width remaining at 0.1 K.

We have also shown in Fig. 1 the lattice constants of the 22-K films as a function of dose. The lattice is seen to expand from the unirradiated value of 5.138 ± 0.004 Å to 5.19 ± 0.03 Å for a dose of 2×10^{17} cm^{-2}. The large lattice parameter[11] (5.168 Å) of bulk *A*15 Nb-Ge was the prime indicator that the as-grown compound was nonstoichiometric,[12] and this condition was subsequently taken as the reason[13] for the low T_c. Our results show that stoichiometric Nb_3Ge can be made to have a larger lattice parameter by introducing defects rather than compositional changes (the ^{4}He particles do not stop in the film), and that when the bulk lattice parameter of 5.168 Å is reached one obtains the bulk T_c (~6 K). (There exists no evidence from x-ray data for appreciable second phase in the films before or after irradiation.) The large lattice-parameter expansion, which results from the damage, correlates with the reduction in T_c in a manner which is at least qualitatively similar to that observed in the as-grown films.[4] It should be noted that Arnold, Krefft, and Norris[14] have shown that 100-keV ^{4}He bombardment of single-crystal sapphire (the same substrate material as used in this study) can produce a maximum lattice-parameter expansion of 0.5%. To check that the swelling of the Nb_3Ge was due to defects and not simple substrate expansion, we determined the lattice parameter of a 3000-Å Nb film on sapphire before and after a 2-MeV ^{4}He bombardment of 1×10^{17} cm^{-2}. There was no discernible increase in the Nb lattice parameter, indicating that the increase in the Nb_3Ge lattice parameter is indeed due to the incorporation of defects.

Sweedler, Schweitzer, and Webb[7] have shown that the increase in lattice constants in the Nb-based *A*15 compounds after neutron damage can be explained in terms of the Nb atoms occupying *B* sites. Experimentally, we find that at high ^{4}He doses all x-ray lines above the 211 reflection become very weak. Calculations show that simple antistructure defects (but retaining a perfect lattice) will not lead to the observed behavior.

The sample with ^{4}He dose of 2×10^{17} cm^{-2} ($T_c = 3.8$ K) was subsequently annealed for 6 h at

750°C and thus found to have a T_c onset of ~15.2 K. No attempt was made to determine the effect of different annealing times or temperatures.

The lower curve of Fig. 1 shows the dose dependence of a film which had an initial undamaged T_c of 9 K (this low-T_c film was prepared under nonoptimum deposition conditions in that the substrate table was run ~50°C below the optimum temperature for high-T_c deposition). It is not possible to distinguish a plateau region in this T_c-dose curve; rather T_c decreases slowly with dose until the saturation value of 3.5 K.[15] Concerning the shape of the T_c-dose curves, we suggest that the plateau region ($< 5\times10^{15}$ cm^{-2}) for the high-T_c films is where those defects introduced by bombardment are at a considerably lower level than the natural background of defects in the film. T_c then degrades with dose when the bombardment-induced defects become dominant. In this region the T_c-dose curve for the 9-K film is then consistent with that of the 22-K films if we assume that films of the same T_c have equivalent defect contributions. For example the 9-K undamaged film is assumed to behave similarly to a 22-K film after a ^{4}He dose of 2.8×10^{16} cm^{-2}. Thus, starting at the same T_c—no matter how achieved—additional bombardment will produce roughly the same decrease in T_c.

The shaded band in Fig. 2 shows the previously reported[4] T_c–resistance-ratio correlation for about 130 films. This correlation band was obtained by plotting data points irrespective of the conditions of the film deposition (such as substrate temperature, etc.), film thickness, and even chemical composition through the Nb/Ge range 2.4–5.5. Superimposed on this correlation band are the resistance ratios of the initially high-T_c films, after ^{4}He bombardment. They lie nicely within the correlation band. This is, again, persuasive evidence that the defects produced during ^{4}He bombardment are similar in their effect to those produced during the film growth process. Some correlation with bulk behavior is evident here. We have measured the resistance ratio of bulk (arc-cast) Nb_4Ge which is single-phase $A15$ structure. (Bulk Nb_3Ge is not a single-phase material.) The bulk Nb_4Ge has a resistive T_c onset of ~7 K with width ~1 K, a lattice parameter of 5.168 ± 0.003 Å, and a resistance ratio of $\rho(300\text{ K})/\rho(25\text{ K}) = 1.2\pm0.05$. The resistance ratio for comparable T_c and (with less precision) lattice parameter in the films obtained either by nonoptimum deposition conditions, nonstoichiometry, or with radiation damage is 1.1 ±0.05. Although the agreement of bulk and film behavior is not precise, the bulk data do indicate considerable defect scattering.

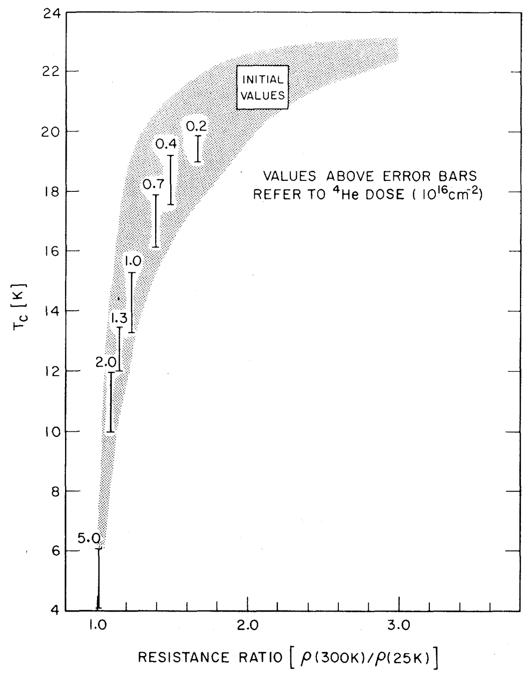

FIG. 2. Resistance-ratio correlation band for 130 as-grown films with the values for damaged films superimposed.

We have addressed ourselves in this work to the specific subject of defects in Nb-Ge thin films. It is possible to introduce, by ^{4}He bombardment, defects into the films that lead to physical behavior very similar to that produced during the growth process. This is demonstrated by the correlations of T_c with resistance ratio, lattice parameter, and critical current.[16] It was shown in our previous work[4] that T_c is not critically dependent on exact stoichiometry. Furthermore, the compositional dependence of T_c led us to question[4] a simplified disorder argument where nonstoichiometric compounds contain simple antistructure defects which lower T_c by interrupting the Nb chains.

The results of this study add some support to our initial suggestion that the high T_c's are critically dependent on the elimination of some defect but its nature is still not known. Bachner and Gatos,[17] Varma, Phillips, and Chui,[18] and Phillips[19] have suggested the possible importance of vacancies for the $A15$ compounds, but it is difficult to identify point defects with certainty. Our x-ray data suggest, however, that the defect may be the loss of translational symmetry of the lattice with microscopic strains occurring over dimensions of the order of some unit cells. While we cannot identify the dominant defects, it would appear that the thin-film growth process minimizes those defects that may be partly responsible for bulk NbGe having a T_c of some 6 K.

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States in the Gap in Glassy Semiconductors

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A model is discussed which for the first time provides a unified description of many electrical and optical properties of chalcogenide glasses. It is proposed that localized gap states are at dangling bonds, and that lattice-distortion effects are sufficiently strong that these states exhibit an effective negative electron-electron correlation energy.

In noncrystalline semiconductors, it is known that localized states in the gap determine many of the electrical properties. For example, the work of Spear on amorphous silicon shows them to be responsible for the pinned Fermi energy, recombination in photoconductivity, variable-range hopping, and observation of ESR.[1] Spear proposes that divancancies are present which have properties similar to those in the crystal.[2] This defect acts either as a deep donor, or as an acceptor lying at higher energy in the gap. The separation between the two states is the Hubbard correlation energy.

The situation in chalcogenides is different. Neither an ESR signal,[3] Curie paramagnetism at low temperatures,[4] nor variable-range hopping[5] has yet been observed. Despite this, ample evidence that these materials contain high concentrations of defect states comes from photoluminescence,[6-8] field effect,[9] photoconductivity,[10] drift mobility,[11] and a pinned Fermi energy.[5] Several different energy levels have been suggest-