# Superconducting transition temperature of ion bombarded niobium carbide surface layers

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The influence of Ge and C ion irradiation on the critical temperature of NbC layers obtained by the diffusion of C onto Nb–Ge–Cu substrate was studied. As a result of the irradiation with Ge ions of 150 keV and fluxes of  $2.10^{15}$  and  $2.10^{16}$  ion cm<sup>-2</sup>, a slight decrease of the critical temperature, of 0.3 K and 0.6 K respectively, was observed. In both cases the critical temperature reached the pre-irradiation values after a thermal treatment for 24 h at 600° C. The irradiation with C ions of 170–180 keV and fluxes up to  $2.10^{16}$  ions cm<sup>-2</sup> led to an increase by 30% of the critical temperature at low energies and to its degradation after the thermal treatment.

## 1. Introduction

Niobium carbide is one of the high temperature superconductors with the B-1 (NaCl type) crystal structure, showing a low transition temperature  $T_c$ where prepared in bulk form by using conventional melting methods. The  $T_c$  depression is correlated with a deficiency of carbon component by the melting process. The maximum carbon content obtainable by conventional methods is 0.98, corresponding to the critical temperature of 11.1 K, the maximum noticed up to now for this compound.

The difficulty of getting the stoichiometric compound is caused by high values (2-24%) of carbon vacancies appearing at high temperatures  $(1400-2000^{\circ} \text{ C.})$  at which the compound is realized. Previous studies [1] have shown that the critical temperature of NbC crystals implanted with C-ions of 200 and 800 keV energy and  $5 \times 10^{16}$  ions cm<sup>-2</sup> flux, followed by an annealing process at  $1200^{\circ}$  C (the optimum temperature for the thermal treatment), was raised by up to 11.8 K.

The present work investigated the possibility of increasing the critical temperature of NbC layers obtained by the diffusion of carbon into substrates made of Nb–Ge–Cu alloys.

## 2. NbC irradiated with Ge-ions

The starting material, Nb–Ge–Cu alloy obtained by the method previously described [2], was laminated and annealed for 5 h at 800° C. During annealing in a graphite crucible, the sample covered itself by a layer of NbC, realized by the diffusion of C from the crucible.

The X-ray pattern confirmed the existence of NbC, the only diffraction lines to appear with those of the copper matrix being the diffraction lines of this compound. After another lamination and annealing for 24 h at  $950^{\circ}$  C, the transition temperature was 11.3 K (Fig. 1).

Layers were implanted at room temperature bombarded with two different fluxes of Ge<sup>+</sup>-ions:  $2 \times 10^{15}$  cm<sup>-2</sup> and  $2 \times 10^{16}$  ions cm<sup>-2</sup> of 150 keV energy.

The X-ray pattern did not indicate the appearance of the compound  $Nb_3$  Ge, the only diffraction lines appearing, together with those of copper, being again those of the compound NbC. The values of the critical temperature obtained after the irradiation are shown in Table I.

In Fig. 2, the  $\rho/\rho_n$  values (where  $\rho/\rho_n$  represents the ratio between the resistivity at a certain temperature and that of the normal state) are



Figure  $l \rho/\rho_n$  as a function of temperature for NbC layers on the Nb-Ge-Cu substrate after lamination and annealing.

plotted against temperature for samples irradiated with a flux of  $2 \times 10^{15}$  cm<sup>-2</sup> Ge ions, and in Fig. 3, for samples irradiated with  $2 \times 10^{16}$  ions cm<sup>-2</sup>.

It can be seen that as a result of the irradiation a slight decrease of  $T_c$  appears (0.3 K for  $2 \times 10^{15}$ ions cm<sup>-2</sup> and 0.6 K for  $2 \times 10^{16}$  ions cm<sup>-2</sup>) which was remedied,  $T_c$  reaching the value held before the irradiation, in both cases, after a thermal treatment for 24 h at 600° C.

Annealing at higher temperatures (650 and  $700^{\circ}$  C) both for shorter time intervals (3 h) and longer time intervals (42 h) led to values of critical temperature even lower than that obtained as a result of the irradiation.

In conclusion, for the samples of NbC obtained

TABLE I Critical temperature of Ge-ion irradiated NbC

Anneal	Duration	$\phi(\mathrm{cm}^{-2})$	Critical temperature	
(° C)	(h)		(K)	
_		0	11.3 ± 0.1	
_	_	$2 \times 10^{15}$	$11 \pm 0.1$	
	_	$2 \times 10^{16}$	$10.7 \pm 0.1$	
600	24	$2 \times 10^{15}$	$11.3 \pm 0.1$	
600	24	$2 \times 10^{16}$	$11.3 \pm 0.1$	
650	3	$2 \times 10^{15}$	$10.2 \pm 0.1$	
700	3	$2 \times 10^{16}$	$10.4 \pm 0.1$	
700	42	$2 \times 10^{15}$	10.9 ± 0.1	

by the diffusion of C on Nb–Ge–Cu alloy substrate, irradiation with Ge-ions does not increase the critical temperature; in fact the irradiation produces a decreasing of the critical temperature. After annealing for 24 h at 600° C the critical temperature increases to the value of non-irradiated material.

Also, one can conclude that, although the substrate is made of an alloy containing Nb and Ge, the implantation of Ge-ions did not lead to the appearance of the compound  $Nb_3Ge$ .

#### 3. NbC irradiated with C-ions

The starting material was the alloy  $Cu_{90}Nb_{6.5}Ge_{3.5}$ obtained in a graphite crucible in an argon atmosphere at 1800° C (1 h), then cooled down by by 40° C s<sup>-1</sup>. A superconducting material resulted with  $T_c = 6.5$  K and the "onset" at 8 K. A lamination with the thickness reduction from 1 to 0.25 mm led to the disappearance of the superconductivity at temperatures higher than 4.2 K.

As a result of an annealing for 5 h at 800° C a



Figure  $2 \rho/\rho_n$  as a function of temperature for NbC layers on the Nb–Ge–Cu substrate after irradiation with Ge ions of flux  $2 \times 10^{15}$  cm<sup>-2</sup> and after annealing. (Curves: • after irradiation; × after annealing at 650° C for 3 h; and • after annealing at 600° C for 24 h.)



Figure  $3 \rho/\rho_n$  as a function of temperature for NbC layers after irradiation with Ge ions of flux  $2 \times 10^{16}$  cm<sup>-2</sup> and after annealing. (Curves: • after irradiation; × after annealing at 700° for 3 h; and • after annealing at 600° for 24 h.)

superconducting material with  $T_c$  of 9.5 K was obtained (Fig. 4, curve 1). The X-ray pattern indicated only the lines of NbC together with those of copper.

A further lamination with the thickness reduction from 0.36 mm to 0.09 mm followed by annealing for 48 h at 950° C resulted in a decrease of critical temperature  $T_c$  down to 7.8 K (Fig. 4, curve 2). This material was irradiated with C-ions of energies: 170, 175 and 180 keV and fluxes  $5 \times 10^{15}$  and  $2 \times 10^{16}$  ions cm<sup>-2</sup>. The values of critical temperatures are given in Table II.

In Fig. 5 the curves  $\rho/\rho_n$  as a function of temperature for NbC are represented. It is noticeable



Figure  $4 \rho/\rho_n$  as a function of temperature for NbC layers on the Nb-Ge-Cu substrate before irradiation; (1) - after an initial lamination and annealing, (2) - after a supplementary lamination and annealing at 950° C for 48 h.

that the implantation of C ions with an energy of 170 keV and a flux of  $2 \times 10^{16}$  ions cm<sup>-2</sup> resulted in the highest critical temperature 10.2 K, which decreases, nevertheless, down to 9.8 K after annealing for 5 h at 800° C.

The irradiation with ions at higher energies resulted in a decrease of critical temperatures even if the flux was maintained. An energy of 180 keV produced a material having superconducting islands with transition at 9.9 K.

The X-ray pattern of this material characterizes itself by the diffraction lines of NbC of lower



Figure 5  $\rho/\rho_{\rm n}$  as a function of temperature for NbC layers on the Nb-Ge-Cu substrate after irradiation. (Curves:  $\times E = 170 \,\text{keV}, \ \phi = 2 \times 10^{16} \,\text{cm}^{-2}, \ \circ E = 180 \,\text{keV}, \ \phi = 5 \times 10^{15} \,\text{cm}^{-2}$ ; and  $\bullet E = 170 \,\text{keV}, \ \phi = 2 \times 10^{16} \,\text{cm}^{-2}$  annealed at 800° C for 5 h.

TABLE II Critical temperature of C-ion irradiated NbC

Anneal temperature (° C)	Duration (h)	φ(cm <sup>-2</sup> )	<i>E</i> (kV)	Critical temperature (K)
_	~-	0	0	7.8 ± 0.1
_		$5 \times 10^{15}$	180	9.9 ± 0.1
-		$2 \times 10^{16}$	170	$10.2 \pm 0.1$
		$2 \times 10^{16}$	175	9.5 ± 0.1
800	5	2 × 10 <sup>16</sup>	170	9.8 ± 0.1

intensity in comparison with those of the sample irradiated with 170 keV having  $T_c = 10.2$  K (Fig. 5).

The lattice parameter increases as a result of the irradiation due to the introduction of supplementary C-ions into the lattice. With these results it is possible to conclude that the irradiation of NbC layers with C-ions led to the increase of the critical temperature, confirming the results given in [1]. The highest value was obtained for the energy of 170 keV and a flux of  $2 \times 10^{16}$  ions cm<sup>-2</sup>. Longer annealing time, higher temperature and higher energies of ions give depressions of critical temperature.

#### References

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Received 28 February and accepted 13 March 1984