JOURNAL OF MATERIALS SCIENCE 17 (1982) 1591–1594

The effects of quenching just after deposition for metastable compounds

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It has been demonstrated that high rate d.c. magnetron sputtering can easily prepare materials such as Nb_3Ge and Nb_3Si in a metastable state. This sputtering-system was made in an effort to stabilize the metstable phases. Specimens were quenched just after sputtering from 1100° C to liquid N_2 temperature at the rate of 3500° C min^{-1}. The relation between quenching rate and superconducting onset temperture, T_{c0}, the transition width, ΔT_c, and the lattice constant, a_0 were examined. The results show that quenching just after sputtering is very useful in preparing metastable materials.

1. Introduction

Gavaler [1] found a superconducting Nb_3Ge with a superconducting onset temperature, $T_{c0} = 22.3$ K which was made by a sputtering in high Ar pressure; a high T_{c0} was also observed by Testardi [2], for the same material, who attained $T_{c0} = 22.3$ K. Recently Paidassi *et al.* [3] obtained Nb_3Ge with $T_{c0} = 23.6$ K by chemical vapour deposition.

A-15-type high T_c films such as Nb_3Ge and Nb_3Si are not prepared in a stable state but in a metastable state. In particular Nb_3Si is expected by extrapolation to have a much higher T_{c0} (25 to 38 K) [4, 5]. This material has been extensively investigated by many researchers [6, 7] and by various methods. However, the preparation of A-15 Nb_3Si with a high T_{c0} seems to be much more difficult than that of A-15 Nb_3Ge.

Our opinion [8] is that the sputtering technique is still promising for the formation of metastable compounds because vapour quenching may result in a faster cooling rate. The only shortcoming of the sputtering method is the possibility of creating an undesirable stable phase during the slow cooling of the film after the deposition.

D.c. magnetron sputtering was done in a sputtering chamber which consisted of a container full of liquid N_2. Samples were quenched just after sputtering by thermal conduction by the sample holder which is tightly fixed on a container keeping liquid N_2 temperature all the time. In this case, the highest quenching rate was about 4000° C min^{-1}. This process freezes the atomic diffusion by shortening the solidification time.

By varying the quenching speed, we measured the change of the transition width, ΔT_c, a_0, and T_{c0}. The existence of a correlation between these parameters has become clear. Judging from the secondary-electron-images taken by an electron probe microanalyser (EPMA), Nb_3Si is more unstable than Nb_3Ge as is theoretically expected.

Nb_3Ge [9] has easily been prepared with a T_{c0} above 22 K, over a wide range of Ar pressure (0.1 to 0.5 torr) and substrate temperature, T_D, (600 to 750° C) by deposition of short duration (20 min). Nb_3Si [8] with $T_{c0} = 17.3$ K and $T_c = 16.4$ K, which is the highest of our samples, has also been obtained.

2. Experimental procedure

2.1. Apparatus

A schematic diagram of the apparatus and a photograph of the sputtering chamber are shown in Fig. 1 and Fig. 2 respectively. D.c. magnetron sputtering was done in a sputtering chamber whose wall is that of a liquid N_2 container (F). The innerwall of the container plays two important roles: (a) it acts as a cryopump to purify the environment. The shape of the sample holder is designed to getter impurity gases effectively by

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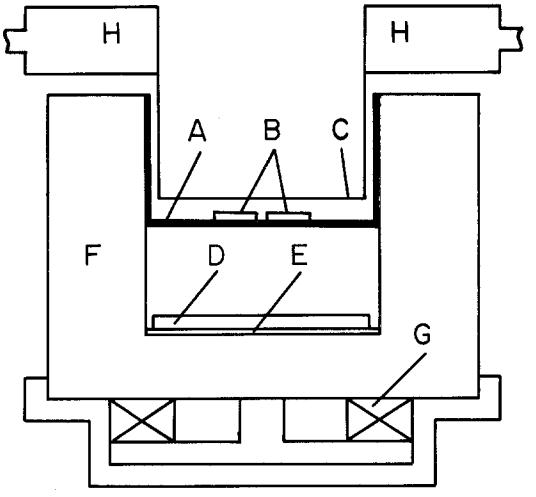

Figure 1 A schematic diagram of an apparatus by which the quenching of a sample just after deposition is possible, showing A: sample holder, B: sapphire substrate, C: niobium heater, D: target, E: insulator, F: coolant (liquid N_2 can), G: magnet and H: heater holder (water cooled).

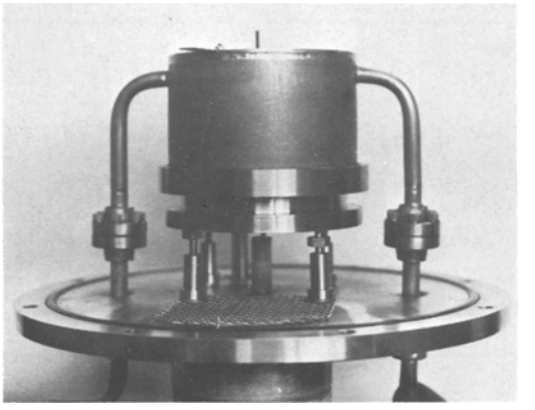

Figure 2 Photograph of a sputtering chamber.

putting a lid on the sputtering chamber. (b) the surface of the bottom cools down a target (D), which helps to increase the sputtering rate and suppress the out-gas from it. In addition the sputtering of materials with low melting temperature is possible.

The target is insulated from the container by an alumina thin plate (E). The Nb heater (C) is connected with the holder and is cooled by flowing water. A cylindrical Lanthanum magnet (G) supplies a magnetic field parallel to the target.

It should be emphasized that this apparatus is furnished with a system to quench samples just after deposition. The sample holder, tightly fixed on the liquid N_2 container by screws to make good thermal contact, plays an important role. Even though the quenching rate is not very high, this system is apparently effective in forming metastable compounds.

Fig. 3 shows quenching characteristics. The temperature of a substrate starts to decrease from the moment that the current (approximately 200 A) flowing through the heater is cut. The quenching rate depends on the level of liquid N_2 in the container; therefore the rate was controlled by it. In addition the initial rate of decrease of temperature is determined by the starting temperature. If the quenching was started at a temperature of 1200° C, a rate of decrease of 4000° C min^{-1} was obtained.

The diameter of the inner and outer cans and their height are, respectively, 60 mm, 115 mm and 70 mm and the diameter of the target is 50 mm.

2.2. Sample preparation and the effects of quenching

A vacuum-system was pumped down to approximately 5×10^{-7} torr by use of an oil diffusion and a rotary pump.

A small amount of liquid N_2 was introduced into the container to protect the magnet from heating and then the temperature was raised by passing a heater current until a temperature sufficient to degass the substrate was obtained. After this process Ar gas with 99.999% purity was introduced into the bell jar.

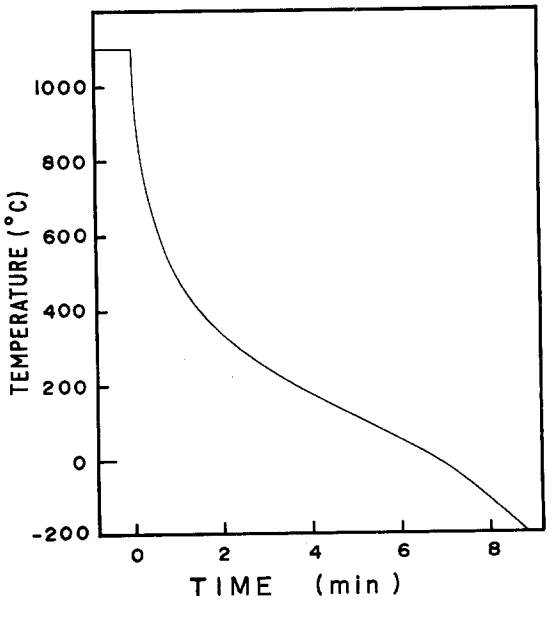

Figure 3 The quenching characteristics.

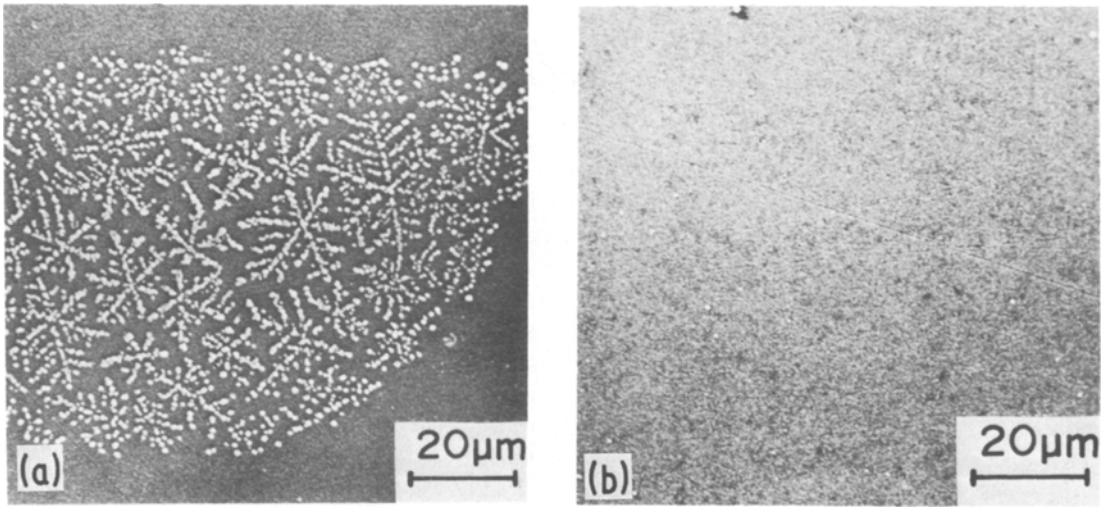

Figure 4 Surface analysis by EPMA, the photograph shows a secondary electron pattern of Nb_3Ge (a) when the sample was cooled down slowly at 40° C min^{-1}, and (b) when the sample was quenched at 2000° C min^{-1}.

Replenishment of liquid N_2 was continued, until the container was full. Presputtering for 10 min was started under the following conditions; sputtering current, $I_P = 150$ mA, applied voltage, $V_P = 350$ V, substrate temperature, $T_D = 740°$ C and Ar pressure, $P_r = 0.8$ torr.

A compound target with a Nb/Ge ratio of 2.5 and a composite target were used for Nb_3Ge and Nb_3Si preparation respectively. Then a shutter was opened for twenty minutes while the container was kept full of liquid N_2. Consumption of liquid N_2 during the deposition time was 0.3 dm^3 min^{-1}.

Immediately after the end of the sputtering, samples were quenched down to −194° C with several quenching rates, ranging from 2500° C min^{-1} to 40° C min^{-1}. The substrates were polished sapphires.

Superconducting measurements were done by a four terminal method.

The quenching-rate-dependence of T_{c0}, ΔT_c and a_0 was examined by using a Au–0.7 wt% Fe–Chromel thermocouple calibrated by a GaAs temperature-standard (Lake Shore Instrument) and an X-ray diffractometer. Surface pattern and composition of the films were measured by EPMA.

3. Results and discussion

Fig. 4(a) shows the second-electron-image of EPMA when a sample was cooled down slowly at 40° C min^{-1}. Large dendritic patterns are seen to grow over the surface and are associated with a different quantity of Ge concentration from the background. Such dendritic patterns disappear clearly from the surface of the sample prepared by quenching at 2000° C min^{-1}. (Fig. 4b). The same result was obtained for Nb_3Si [8] and the effect is much more serious.

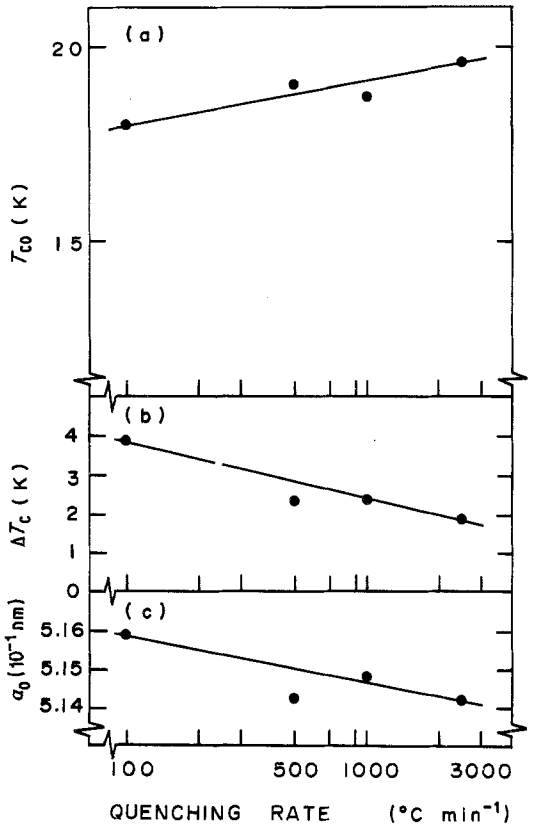

Figure 5 Relation between the quenching rate and T_{c0}, ΔT_c and a_0 when a compound target was used.

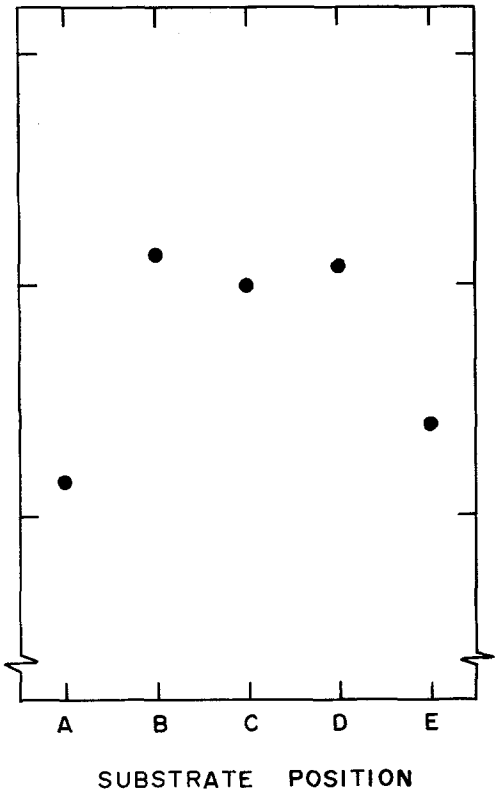

Figure 6 Positional dependence of the Nb/Ge ratio of a sample. The positions noted by A and E are rich in Ge because these points are low in temperature. The heat is absorbed by the sample holder during the deposition resulting in a lower temperature.

We believe that slow cooling of samples just after deposition is responsible for the growth of the undesirable metastable phase because of the diffusion of atoms.

The relationships between T_{c0}, ΔT_c and a_0, and quenching rate are depicted in Fig. 5. With increasing quenching rate, T_{c0} rises and the transition becomes sharp. The lattice constant a_0 decreases.

Fig. 6 shows the ratio of Nb to Ge. In positions A and E the sample is in contact with the edges of the sample holder. This results in low temperature and a low Ge-concentration because the sample-holder absorbed heat during the deposition. Because of above mentioned reason T_c was measured along the centre line of the sample to exclude this edge effect.

In addition, some of Nb_3Si samples which had been made by this apparatus showed remarkable decrease of resistance at 38 K. However, these samples are very unstable and their resistive curve gradually changes by heat cycling when samples are in liquid He to measure T_c. In the present stage of the study, it is not clear whether the superconducting transition or the structural transformation is responsible for this phenomenon. Further study is progressing.

Acknowledgements

The present work was supported partly by a Grant-in-Aid for Scientific Research from the Ministry of Education.

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Received 21 September
and accepted 4 November 1981