BILJEŠKE NOTES

CCA-259 546.28.05:542.14

The Floating-Zone Refining of Silicon by Electron Beam Heating

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Received April 6, 1962

The contamination of a melt caused by the material of the container is completely avoided by the floating zone method. For this reason the method, firstly realized by P. H. Keck and M. J. Golay[1], is nowadays used very often for obtaining various materials of extremely high purity. The method is especially valuable in the case of chemically active melts and certainly it is the best way for obtaining single crystals when extreme purity is primarily required. Zone melting can be achieved by different heating techniques, high frequency being used mostly. Electron beam heating was introduced by A. Calverley *et al.*[2] In the case of materials with very high melting point it has the advantage over high frequency heating. In the present article an improvement of this method as well as details of the equipment and floating zone refining of silicon are described.

The apparatus is shown in Fig. 1. It consists of a cylindrical water cooled metal chamber in which the electron source and the head of the assembly, for mounting a rod shaped sample, are enclosed. The chamber has three openings. Two of them serve for vacuum measurements, the third one for the observation of the melting. It is made of a concave glass window provided with a segment shutter in a fixed position. By turning the window one always exposes the new and transparent part of it, thus enabling the continuous observation of the process. On the assembly head there is a movable frame with two specimen holders coupled through a metal ball socket. The lower holder rests on an elastic spring. Allowance is thus made for any dilatation or contraction of the sample during the heating and cooling periods. Cracking of the sample is thus avoided. The apparatus is equipped with an automatic cycling system requiring only sporadic control. The regulation of the zone height and the final diameter of the sample is achieved simply by rotating the main shaft as it is seen from Fig. 1. The mechanism for moving the whole frame inside the chamber consists of the motor driven gear box. The speed of the zone is therefore adjusted at will from 6 to 16 cm/h. The required vacuum of 10^{-5} torr. is achieved as usually by coupling the rotary oil pump with a three stage oil difusion pump. The whole chamber is mounted on a modified Pollard conduction trap[3] cooled with liquid air.

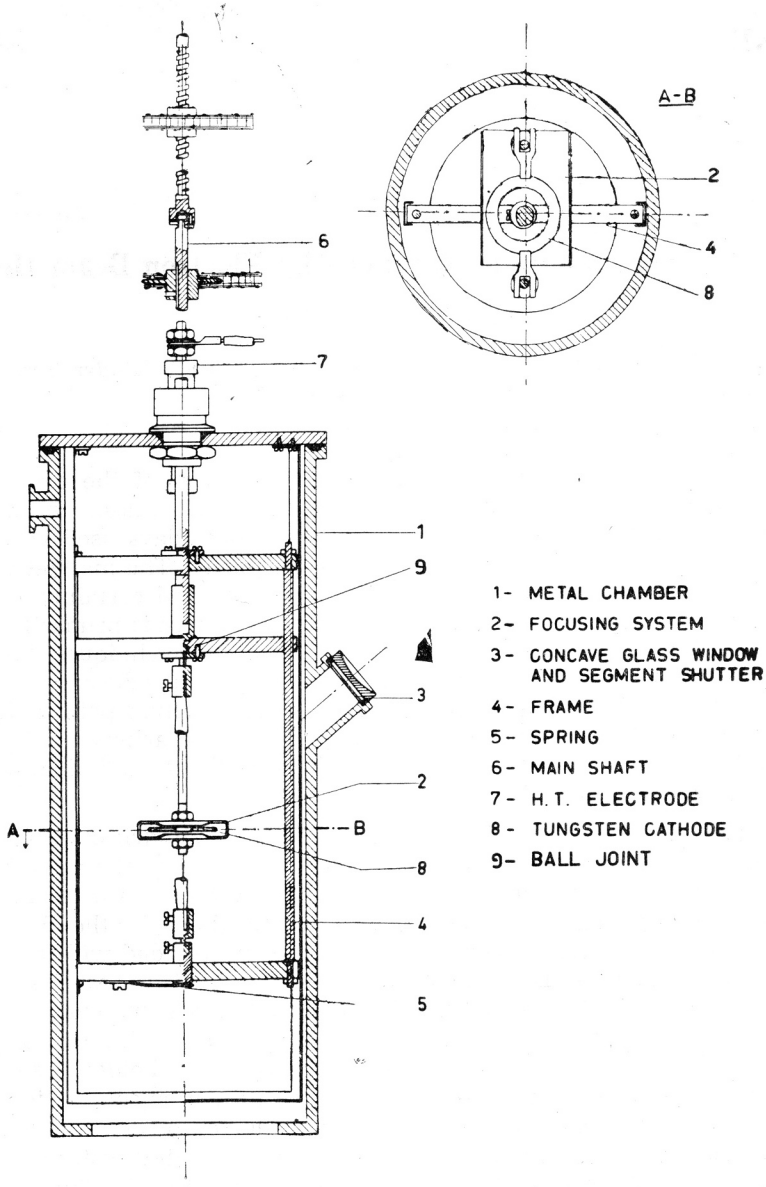

Fig. 1. Bombarding chamber

The emission current is subject to large fluctuations in the course of the process and must therefore be controlled. The controller similar to one described by Calverley and coworkers fullfiled the requirements. The response time of the controller is $^1/_{20}$ sec. The mains voltage is separately stabilized to 1 p. c. The high tension rectifier operates from 0 to 7000 V, with a max. emmision

current of 1000 mA. The equipment is safeguarded by 30 lamps of 100 W connected in series in the high tension line. They serve both as protective resistance and an additional stabilization in the case of sudden large changes of the emmission current that cannot be followed by the controller. A stable melting zone is achieved by adjusting the heating voltage of the cathode and the high tension for the electron acceleration, after which one switches on the automatic control. The circuitry of the latter is given in Fig. 2. After the melted zone reaches the upper end of the sample rod, a relay switches off the cathode heating (or reduces it to a desired level), and reverses the motor. The frame is now traveling at the maximum speed in reverse. When the second microswitch is touched, the cathode heating is switched on again. The same microswitch reverses the motor, and the frame inside the chamber is traveling backwards at the minimum speed, thus repeating the zone melting process.

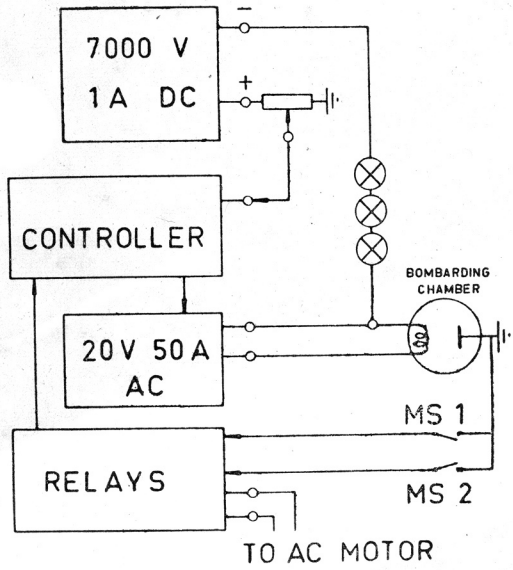

Fig. 2. Electrical circuitry of the apparatus

The described apparatus was used for zone melting of silicon. The samples were prepared from technical grade microcrystalline silicon (Merck). Silicon powder of different granulation was pressed into rods of 100 mm length with a cross section of one cm^2, at 2000 kg/cm^2. One hour sintering followed at a temperature of 1380—1400° C, in a vacuum of $5 \cdot 10^{-5}$ torrs. Spectrographical examination showed markedly a purification effect, which is to be explained by partial evaporation of the admixtures due to the reduction reactions of the type:

$$Si_{(s)} + SiO_{2\,(s)} \longrightarrow 2SiO_{(g)}$$

$$Si_{(s)} + MeO_{(s)} \longrightarrow Me_{(g,\,s)} + SiO_{(g)}$$

The metal and silicon oxide vapors deposit onto the cooler part of the tube. The subsequent floating zone refining removes the remaining nonvolatile

impurities owing to their different distribution coefficients between solid and liquid silicon. By using this procedure we obtained silicon rods (length: 140 mm, mean diameter 10 mm) usually composed of two crystals. On the other hand, when much purer silicon was used (Sylvania, 6—15 ohm. cm) the primarily obtained bicrystalline rod was ground on its end and remounted with this end at the bottom which thus served as a seed for the single crystal obtained during the zone melting process. One such single crystal is shown in Fig. 3.

The resistivities of the obtained single crystals were measured by means of the compensation method, and showed some peculiarities. The minimum resistivity at the bottom part is varying from about 200 ohm. cm. in the center with a sharp increase toward the surface where it is greater then 1000 ohm. cm. Upper sections are showing subsequently lower resistivities, *i. e.* down to 2—3

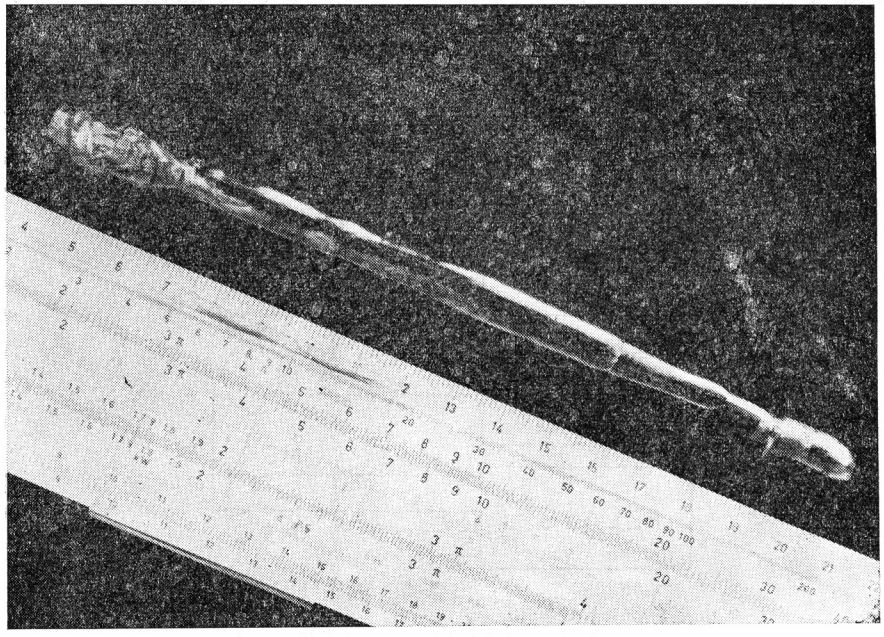

Fig. 3. Silicon single crystal

ohm.cm, with the previously mentioned difference between the core and the surface region. Lower part of the rod was zoned many times more than the upper one because the main purpose of the process was to grow the single crystal. Each time when the growth of the single crystal was interrupted at a certain length from the bottom the process was started again from the beginning. Thus the lower part of the rod was zoned at least 20 times and the top part only once.

The radial efect of the purification is probably due to the preferential evaporation of the impurities owing to the very high local superheating of the molten zone with a very limited stirring.

The method therefore seems to be quite useful for simultaneous production of single crystals and zone purification up to the very high purities, but providing for rotation of the one or both parts of the silicon rod.

The thermoelectric probe showed that the material is of the p-type as it was before the zone melting. If the radial effect of the purification is really due to the above mentioned possible reason it must be expected that the silicon of the n-type could be converted into p-type, because boron is probably the only impurity that cannot be removed neither by zone melting nor by the preferential evaporation.

Acknowledgment: The authors are greatly indebted to Prof. Dr. D. Grdenić for his stimulating interest and revision of the manuscript. Thanks are due to Dr. S. Šćavničar, who proposed this work, and to Dr. B. Kamenar for helpful discussions and encouragement as the work proceeded. We express our gratitude to Mr. R. Mutabžija for the construction of the controller.

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IZVOD

Čišćenje silicija u lebdećoj zoni taljenjem pomoću snopa elektrona

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Prikazana je konstrukcija i način rada automatskog uređaja za zonalnu rafinaciju i rast monokristala metodom ledbeće zone. Rastaljena zona se dobiva pomoću fokusiranog snopa elektrona.

Opisana je metoda priređivanja sintrovanih štapova od silicija u obliku praška, što se općenito smatra ozbiljnim problemom u tehnologiji poluvodiča.

Uređaj je opremljen automatskim sistemom za kontrolu elektronske emisije i ponavljanja procesa taljenja tako da zahtijeva samo povremenu kontrolu. Eksperimenti su izvedeni taljenjem silicija i dobiven je monokristal dužine 110 mm, promjera oko 8 mm.

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ZAGREB

Primljeno 4. travnja 1962