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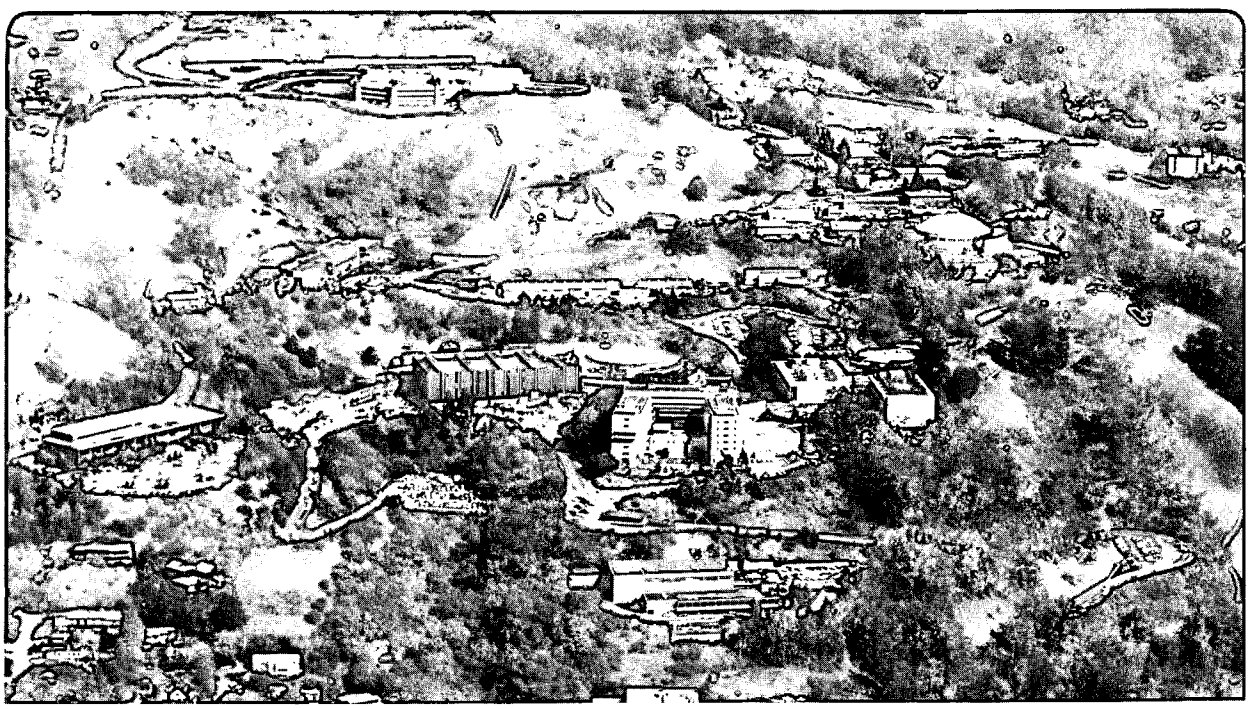

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EXTRINSIC GERMANIUM PHOTOCONDUCTOR MATERIAL: CRYSTAL GROWTH AND CHARACTERIZATION

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Abstract

Ge:Ga and Ge:Be extrinsic photoconductors are used in the 50 - 200 and 30 - 50 μm wavelength range respectively as optimized detectors for far-infrared astronomy applications. Reproducible materials synthesis and comprehensive materials characterization are required for the development of focal plane detectors which reach the high sensitivity which is theoretically possible under the very low background flux conditions of space-based observation. Ge:Ga, Ge:Be, and Ge:Zn photoconductor materials have been grown using the Czochralski technique under high purity conditions. Residual impurities can be controlled to levels of $\sim 10^{10}$ cm^{-3}, leading to greater control of free carrier lifetime and mobility, and more reproducible detector performance. Characterization of the material with variable temperature Hall effect and infrared spectroscopy shows that Be- and Zn-doped crystals grown under a H_2 atmosphere can contain hydrogen-related complexes which affect detector performance by decreasing the resistivity of the material at low temperatures. The growth of Ge:Be presents a special case in which the oxygen content of the melt environment is a critical factor in determining reproducibility of Be doping and device performance.

Introduction

The development of extrinsic Ge photoconductors for the 30 - 200 μm wavelength range requires a basic understanding of material properties and the ability to characterize and reproducibly synthesize single crystal material. Current interest in extrinsic Ge photoconductors is driven primarily by new opportunities, both in Europe and the United States, for space-based telescopes. These telescopes operate with very low background photon fluxes. As a result, there is a need for more sensitive detectors to reach the background limited performance which these telescopes can, in principle, permit. In addition, it will become increasingly important to have highly reproducible materials properties and device performance for multi-element arrays.

Schematic spectral responses for Ge:Ga, Ge:Be, and Ge:Zn are shown in Fig. 1. The long wavelength cut-off of Ge:Ga can be extended to ~ 250 μm with the application of uniaxial stress[1]. Extrinsic silicon detectors are available for wavelengths shorter than ~ 20 μm, and doped semiconductor bolometers are the most common detectors for wavelengths longer than 200 μm.

This paper will review the use of Czochralski crystal growth for the preparation of Ge:Ga, Ge:Be and Ge:Zn IR detector material. The effects of primary and residual doping on detector performance will be presented.

Czochralski Crystal Growth

Doped single crystal Ge for IR detectors is generally prepared either by Czochralski growth from a doped melt or by a zone leveling technique. We will discuss here only results we have obtained with Czochralski growth, although zone leveling techniques, especially for special dopants such as Be or Zn, are very common. Bulk doping of these materials by diffusion is impractical since the high temperatures required for diffusion of substitutional impurities such as Ga, Ge, and Zn will also lead to serious contamination with fast diffusing interstitial impurities such as Cu.

The primary benefit of the use of Czochralski crystal growth is the excellent control of both crystallography and residual impurity concentrations. High purity single crystal Ge with residual, electrically active net impurity concentrations of $\sim 10^{10}$ cm^{-3}, is required for the fabrication of nuclear radiation detectors (p-i-n diodes), and crystal growth facilities have been specially developed for this purpose[2]. The "starting charge" is composed of high purity, zone refined polycrystalline germanium. To dope selectively with a single dopant (Ga, Be, or Zn), a small piece of a heavily doped ($p = 10^{18}$ cm^{-3}) "master alloy" is added to the charge. At the concentrations required for conventional IR detectors ($p = 10^{14} - 10^{15}$ cm^{-3}), direct doping with pure metal is very inaccurate. For example, to dope a 1 kg crystal with Ga = 10^{14} cm^{-3} at the seed end would require 0.4 g of a master alloy with $p = 10^{18}$ cm^{-3}, as opposed to 4 μg of metal. Master alloys are characterized by room temperature Hall effect to determine the doping concentration.

One factor that must be considered in Czochralski growth of detector material, which is not an issue with floating zone or zone leveling techniques, is the segregation of the dopants along the length of the crystal. The segregation profile (doping concentration as a function of distance) is a function of many factors: the individual dopant, the growth rate, and, as will be discussed, the type of atmosphere in which the crystal is grown. Because of this segregation behavior, it is possible that only a part of the crystal will have the proper range of doping for the desired application.

Ge:Ga

Gallium-doped germanium is the most widely used extrinsic Ge material. The materials development and availability of Ge:Ga was greatly aided by the fact that Ge:Ga was used as a starting material for Li-drifted nuclear radiation detectors before high purity Ge was available for this purpose. Standard Ge:Ga which is available commercially for IR detectors generally has [Ga] $\cong$ 10^{14} cm^{-3} with a compensating donor concentration ranging from 1 - 5 x 10^{12} cm^{-3}. This type of material has a breakdown voltage of 3 - 4 V/cm at 3.0 K and has been extensively characterized[1,3,4].

The Ga concentration is the most obvious materials parameter. This is not difficult to control since Ga does not form a highly stable oxide, does not have a high vapor pressure, and is not a common contaminant in the crystal growth environment. Optimum doping for a photoconductor is usually determined by a compromise between maximum absorption and minimum "dark current" (i.e. current which is not caused by incident photons). This dark current can arise

from several sources including 1) thermally generated free carriers, 2) hopping conduction, and 3) surface currents. The limit of the acceptable amount of dark current is given by the background photon flux that will be incident upon the device in an astronomy application.

If the dark current in a photoconductor is due primarily to thermally generated free carriers, a large increase in sensitivity is obtained by cooling the device, since the free carrier concentration is exponentially dependent on the temperature. At low temperatures ($T \lesssim 3.5$ K), however, hopping, or impurity related conduction is often the main conduction mechanism in moderately doped semiconductors[5]. The reduction of current due to hopping conduction requires changes in material parameters, since hopping conduction is only weakly temperature dependent.

The absolute concentration of residual donors in high purity Ge can be as low as 10^{10} cm^{-3}. This level of purity is achieved in crystals grown from a SiO_2 crucible under a H_2 atmosphere.

A Ge:Ga detector with a Ga concentration of 10^{14} cm^{-3} and a residual donor concentration of 10^{10} cm^{-3} has a compensation ratio, K, of 10^{-4}. This is two orders of magnitude smaller than the standard material. Detector results from this type of material will be reviewed in a later section.

Ge:Be

A more complicated set of material parameters exists for the case of a photoconductor which has as its primary dopant a semi-deep level such as Be or Zn. In this case, one must be concerned with the concentration of the primary dopant, the concentration of the n-type residual impurities, and the concentration of p-type residual impurities such as B and Al. Although B and Al are also present in Ge:Ga material, the fact that B, Al, and Ga all have similar ionization energies and optical cross sections means that the thermal and optical effects of B and Al are unimportant as long as $[B] + [Al] \ll [Ga]$, a condition that is easily achieved with high purity conditions. In a Ge:Be or Ge:Zn detector, however, variations in the concentration of these shallow levels, even at residual concentrations, will affect the low temperature detector behavior.

Ge:Be crystals were also grown using the Czochralski technique and a Be master alloy. Because Be forms a very stable oxide, this presents a special case in which the oxygen content of the melt environment is a critical factor in determining reproducibility of Be doping. The best control of Be concentration has been achieved by growing the crystals directly from a carbon susceptor under vacuum, to eliminate the SiO_2 crucible and the H_2O in the H_2 gas as sources of oxygen[4,6]. Under these conditions, the doping at the seed end is within a factor of 2 of the calculated value based on the initial crystal charge, and a normal segregation profile is observed. Beryllium in Ge has an equilibrium segregation coefficient of $K = 0.8$[7], and we obtain an effective segregation coefficient of $K = 0.25$ for our growth conditions under vacuum.

Ge:Be crystals for special applications have been grown from a carbon susceptor under a H_2 atmosphere. This change in crystal growth parameters has several effects which are important for detector material. The effect of

the H_2 atmosphere on the Be segregation profile is shown in Fig. 2. As predicted by equilibrium thermodynamics calculations, the H_2O in the H_2 gas reacts with the Be in the melt, leading to depletion of Be in the melt during crystal growth. This results in the flat segregation profile. Although it may be beneficial to have a flat profile (and therefore more material in the desired concentration range), it is difficult to predict what the reduction in Be concentration will be under these growth conditions.

The hydrogen atmosphere also affects the residual shallow acceptor concentration. Beryllium doped crystals grown under a H_2 atmosphere have been shown to contain a novel shallow, hydrogen-related acceptor, A(Be,H)[8]. These are present at a concentration of ~ 1% of the Be concentration, and affect detector performance by decreasing the resistivity of the material at low temperatures. However, the concentration of these centers can be reduced with thermal annealing. The decrease in free carrier concentration that occurs when the H-related centers are annealed results in a change of orders of magnitude of detector resistivity and dark current at low temperatures (see Fig. 3).

Optimum Be concentration for a far-IR detector is 10^{14} - 10^{15} cm^{-3}, depending on operating temperature and photon background. The optimum condition for shallow level doping is to have the concentration of residual donors greater than that of shallow residual acceptors [$N_D \geqslant N_A$ (shallow)], with [N_D], [N_A (shallow)] << [Be]. This provides the highest resistivity and lowest dark current at low temperatures without a major decrease in mobility due to excessive counterdoping.

Ge:Zn

Although Zn does not oxidize as readily as Be, it does have a very high vapor pressure (1.27×10^3 torr at 960°C), and so tends to evaporate from the melt during crystal growth. This depletes the melt of electrically active Zn and causes a flat segregation profile similar to that for depletion of the melt due to oxidation. Growth of material doped with high vapor pressure dopants (Zn, Hg, Cd) is normally done by vapor doping in a sealed capsule[3]. Alternately, a zone leveling technique is used in which the dopant can be added at several points during crystal growth.

Only a small number of Ge:Zn crystals for detector material were grown using the Czochralski technique. There is less practical application for Ge:Zn detectors in astronomy, since they begin to overlap the wavelength range which can be covered by Si:X detectors and since the development of Ge:Be detectors has been quite successful. Zn-doped material grown under a H_2 atmosphere also contains a shallow, hydrogen-related acceptor, A(Zn,H)[8,9]. This has the same effect on detector material as discussed for the Be case. The effect of annealing on the free carrier concentration is shown in Fig. 3.

Deep Levels and Cu Concentration

The presence of deep level impurities or defects in far-IR detector material is not as deleterious to device performance as in the case of a diode or an optoelectronic device. Deep levels will not be electrically active at the low temperatures at which IR devices are operated and will not serve as

recombination centers since we discuss devices with only one type of carrier. It should be noted, however, that deep level spectroscopy studies of the Czochralski-grown detector material indicate that no deep levels are present above a concentration of 10^{10} cm^{-3}, i.e., 1% of the residual shallow level concentration.

Copper contamination is always a problem with Ge, especially for the high purity material required for nuclear radiation detectors. High purity crystal growth facilities are specially designed to eliminate sources of Cu contamination. It can easily be introduced, however, by subsequent high temperature processes, such as the annealing of implanted layers. At temperatures below $\simeq 350°C$, the equilibrium concentration of Cu is less than $\sim 10^{10}$ cm^{-3}, and so annealing of B implanted layers can be accomplished without any significant introduction of Cu. Substitutional Cu is a triple acceptor in Ge, with the shallowest level at 44 meV. Since this is a larger energy than the ionization energies of interest for far-IR detection with Ge:Be or Ge:Ba, the presence of residual Cu will not seriously affect the detector material. The Cu will be electrically neutral and will act primarily as a neutral scattering center to reduce mobility. This effect, however, will be insignificant compared to the scattering by the primary dopant and the charged impurity scattering by the ionized shallow levels.

Detector Performance

Ge:Ga detectors generally achieve responsivities of 1 - 10 A/W at 3.0 K with detective quantum efficiencies of ~ 30% at background fluxes of 10^7 - 10^9 photons/second. At long wavelengths and low backgrounds, however, it is difficult to determine the exact photon signal, and reported quantum efficiencies still vary substantially, even for the same detector in different laboratories. The trends, however, between performance and material parameters are consistent.

The lifetime of the free holes in a Ge:Ga detector is inversely proportional to the concentration of donors in the material. The effect, then, of lowering the donor concentration to a level of 10^{10} cm^{-3} is to increase the free carrier lifetime and the mobility, thus increasing the responsivity by almost two orders of magnitude. The increase in lifetime and mobility also leads, however, to a decrease in the maximum bias which can be applied to the detector before the onset of impact ionization breakdown. Comparisons of detector performance for standard Ge:Ga and ultra high purity material have been published, with methods suggested for further development of material for high responsivity Ge:Ga photoconductors[10].

For Ge:Be detectors, optimum performance of $\eta_d = 46\%$ with a responsivity of 5 A/W has been attained at $\lambda = 42$ μm at a background flux of 10^8 photons/second on the detector[11]. The responsivity of a Ge:Be detector can be strongly temperature dependent when the shallow acceptor levels (B, Al, shallow acceptor complexes) are closely compensated [$N_D \approx N_A$ (shallow)][11-14]. The responsivity has been observed to decrease from 40 A/W in closely compensated Ge:Be as the device temperature is reduced from 4.2 to 2.5 K. This strongly temperature dependent behavior disappears, however, when $N_D \gg N_A$ (shallow) or N_A (shallow) $\ll N_D$. The control of residual impurities in the crystal growth is important then for the control of both the

absolute responsivity and the temperature dependence of the responsivity in a material such as Ge:Be, Ge:Zn, Si:Ga, or Si:In.

Because of the large role that residual shallow levels play in determining the performance of a multi-level photoconductor, the selection of optimized material requires full characterization of the material with regard to both primary and residual dopants. One must determine, based on the temperature of device operation and the background flux levels during observation, whether enhanced responsivity due to close compensation is an important goal, and then select material accordingly[15].

Summary

Ge:Ga, Ge:Be, and Ge:Zn photoconductor materials have been grown using the Czochralski growth technique under high purity conditions. The concentration of residual compensating donors determines both the responsivity and low temperature resistivity for low background far-IR detectors. In Ge:Be and Ge:Zn material, the concentration of both residual shallow acceptors and donors is important in determining the temperature dependence of the responsivity. Hydrogen related shallow acceptors in Ge:Be and Ge:Zn photoconductor material are present at approximately 1% of the primary dopant concentration in crystals grown in a H_2 atmosphere, and greatly reduce the low temperature resistivity. These centers are not present in vacuum grown material. It is necessary, therefore, to control both the crystal growth parameters and the residual, as well as primary doping, in order to have reproducible detector material.

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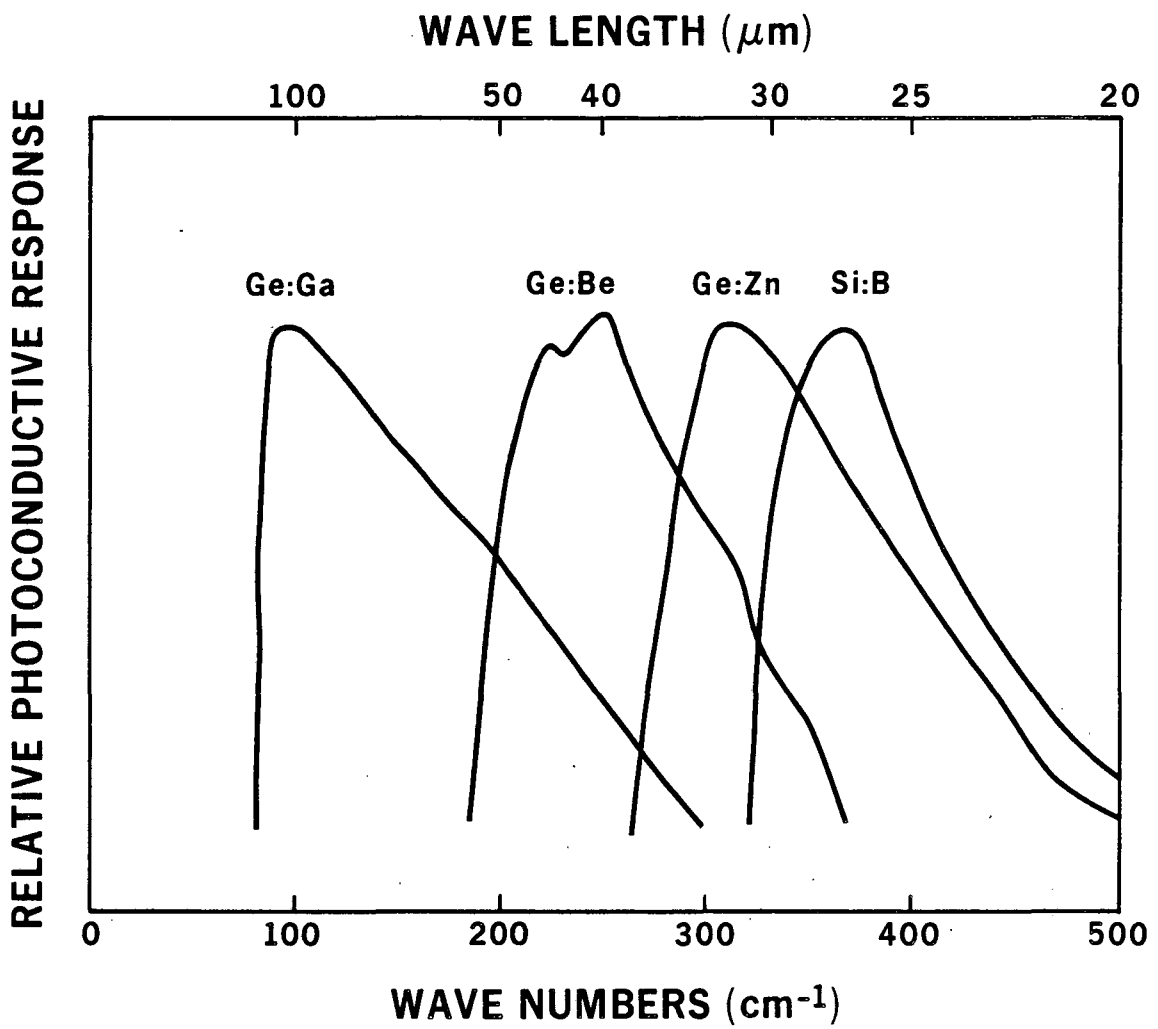

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Fig. 1.

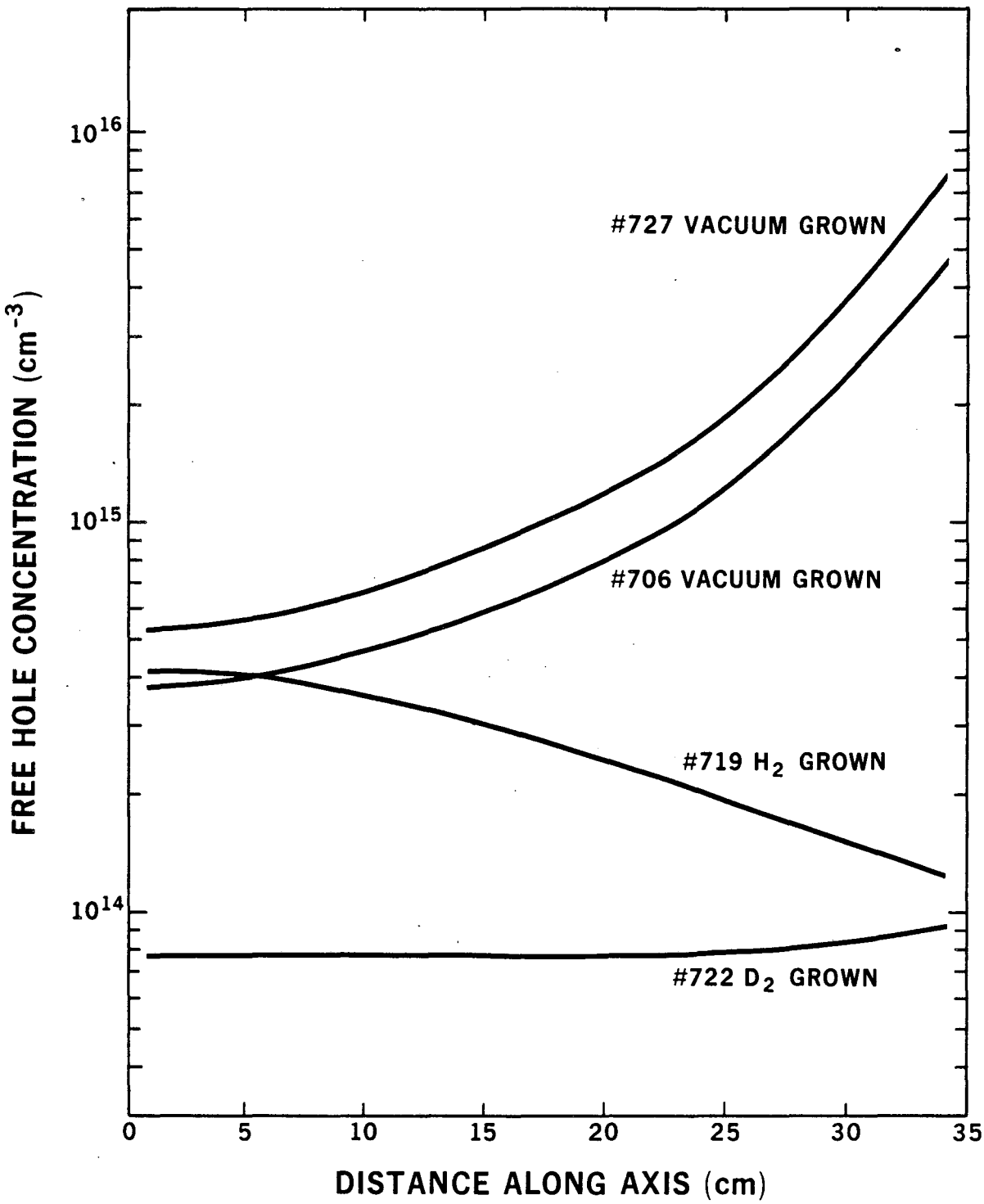

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Fig. 2.

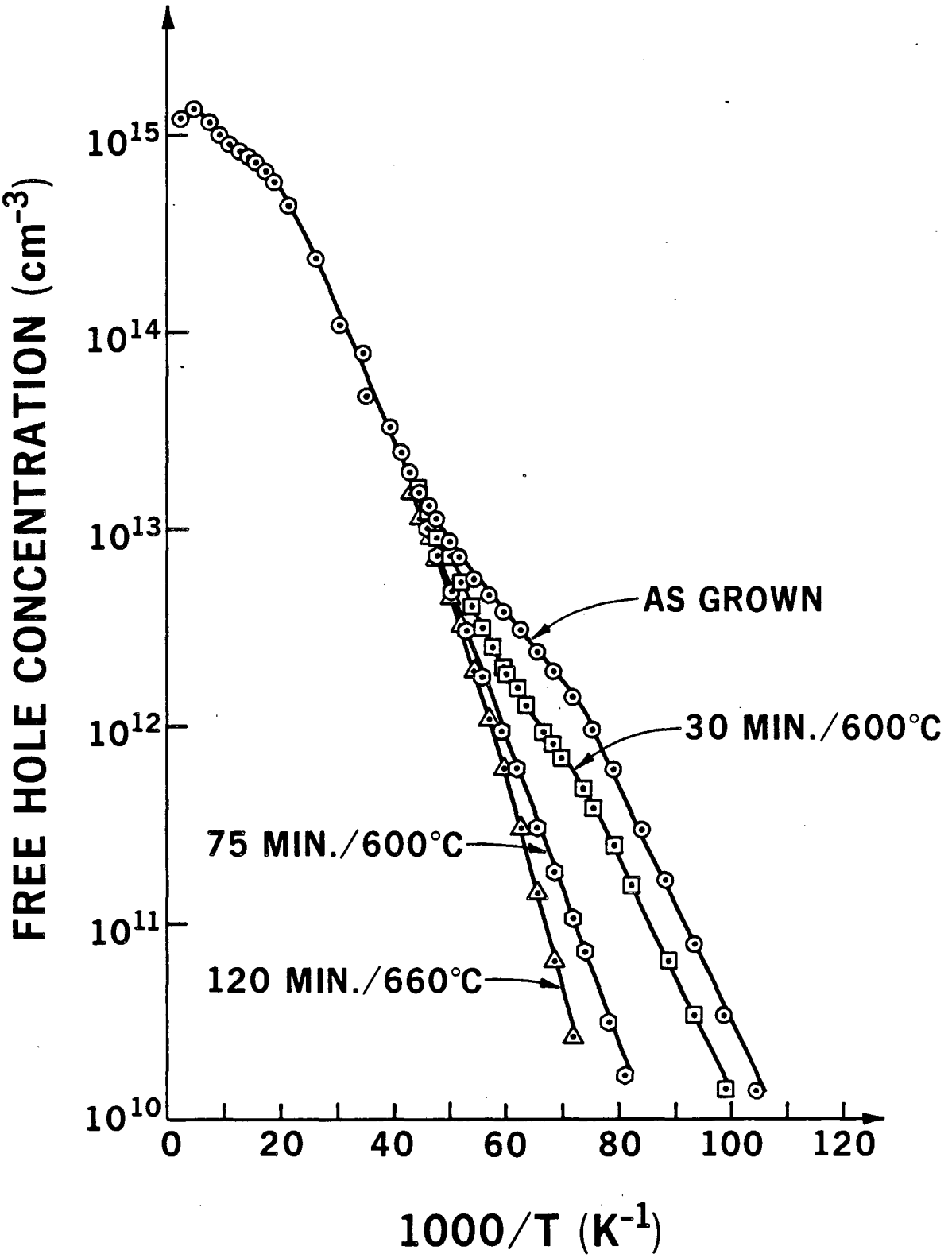

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Fig. 3.

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