LBL--15409

DE83 014863

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

Presented at the 7th International Conference on Infrared and Millimeter Waves, Marseilles, France, February 14-18, 1983; and submitted to the International Journal of Infrared and Millimeter Waves

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February 1983

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

Submitted to the International Journal of Infrared and Millimeter Waves. Results contained in this paper were presented at the 7th International Conference on Infrared and Millimeter Waves, Feb. 14-18, 1983, Marseilles, France.

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*This work was supported by NASA Contract No. W-14,606 under Interagency Agreement with the Director's Office of Energy Research, Office of Health and Environmental Research, U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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Abstract

Ge:Be photoconductors have been developed for low-photon-background applications in the 30 - 50 μm wavelength region. These detectors provide higher responsivity and lower noise-equivalent power (NEP) than the Ge:Ga detectors currently operating in this wavelength range. Beryllium-doped single crystals were grown by the Czochralski method from a carbon susceptor under a vacuum of ~ 10^{-6} torr. We report an optimum detective quantum efficiency of 46% at a background flux of 1.5 x 10^{8} photons/second (7 x 10^{-13} W). Ge:Be detector performance is strongly influenced by the absolute concentrations and the concentration ratio of residual shallow donors and shallow acceptors.

Key words: Photoconductors, Infrared detection, Ge:Be

Introduction

Beryllium-doped germanium photoconductors were first investigated by Shenker et al in 1967[1]. Because Be, a substitutional double acceptor, has a first ionization energy of 24.5 meV and is highly soluble in the Ge lattice (~ $10^{20}cm^{-3}$ at 1200 K)[2], Ge:Be has since been a primary candidate for an optimized photoconductor in the 30 - 50 μm wavelength range. This region is of interest to present and future space astronomy projects which require

far-infrared detectors approaching photon-noise limited operation at low background levels. The development and application of Ge:Be detectors have been hindered, however, by the lack of reliably doped Ge:Be crystals with good crystallography and low residual impurity concentrations.

Crystal Growth and Characterization

Detectors have been produced from several ~ 700 g beryllium-doped Czochralski grown single crystals [long axis parallel to <113>] with low dislocation density (< 1000 cm^{-2}). Use of a high-purity germanium growth facility allowed for excellent control of the shallow residual impurity concentrations. In addition, Czochralski growth results in better crystallography than the zone-leveling technique which has been used by other groups to develop Ge:Be detectors[3,4]. Because beryllium readily oxidizes, however, the use of standard high-purity germanium growth conditions (i.e., silica crucible and H_2 atmosphere) could result in the loss of beryllium acceptors due to the formation of stable BeO from the reduction of either SiO_2 or the H_2O which is present in equilibrium with the H_2.

A calculation following the method used by Darken[5] indicates that the formation of stable BeO would be thermodynamically favorable at the melting point of germanium (1200 K) for a beryllium concentration in the melt of $5 \times 10^{15} cm^{-3}$ for a partial pressure ratio of $p(H_2O)/p(H_2)$ in excess of 6×10^{-7}. Since the lowest ratio generally attained in practice (~ 10^{-5}) could lead to a loss of beryllium acceptors, Ge:Be crystals were grown from a carbon susceptor under vacuum (~ 10^{-6} torr) to eliminate the two primary sources of oxygen. Doping with beryllium was achieved using a heavily doped ($5.5 \times 10^{18} cm^{-3}$) master alloy. Beryllium concentration profiles along the length of the crystals were determined by room temperature resistivity and Hall effect measurements and have been within a factor of two of the calculated estimates based on the weight of the charge and the beryllium concentration in the master alloy.

Figure 1 shows the beryllium concentration profiles for three Ge:Be single crystals. The equilibrium segregation coefficient, K_0, for beryllium in germanium[1,2] has been reported to be 0.07 - 0.08. The profiles indicate an effective segregation coefficient, K_{eff}, of approximately 0.25 for our growth conditions. Since this segregation behavior is also observed for phosphorus ($K_0 = 0.08$, $K_{eff} = 0.25$)

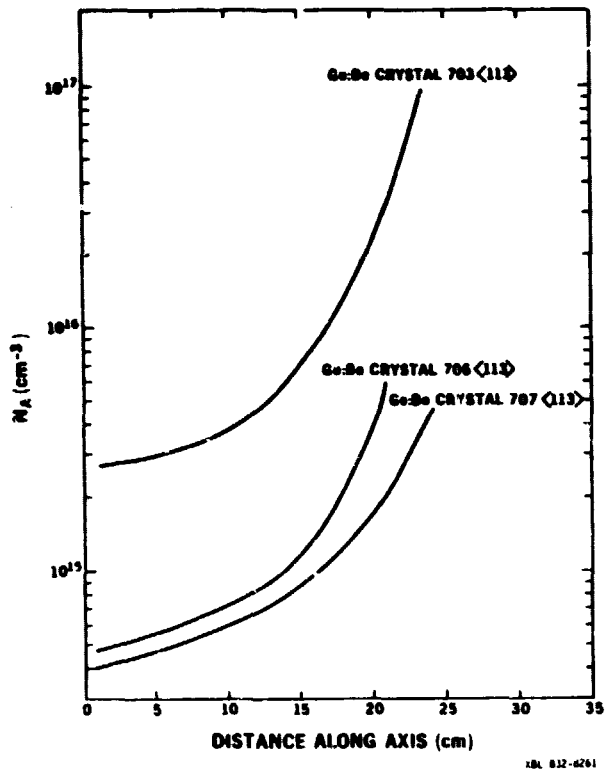

Fig. 1. Net acceptor concentration as a function of distance along the crystal axis.

during the growth of high-purity germanium at the same pull rate and rotation speed, we conclude that this represents the expected segregation of the beryllium and that loss due to the formation of BeO is not a significant factor.

Variable temperature Hall effect measurements (300 - 10 K) were made to determine concentrations of shallow residual acceptors and donors. The starting germanium charges had electrically active shallow donor concentrations $|N_D - N_A| \lesssim 10^{11} - 10^{12}$cm^{-3}. After growth from the carbon susceptor, these crystals had net shallow acceptor concentrations, believed to be due primarily to the activation of aluminum which existed previously as electrically neutral compounds[5,6]. Complete compensation of the shallow acceptors was achieved in one crystal by the addition of a Ge:P master alloy to the charge.

TABLE I. Material Parameters for Ge:Be Photoconductors

Detector	Be Conc. (cm^{-3})	Shallow Majority Levels	Net Concentration of Shallow Levels (cm^{-3})
703- 4.2	$1.3x10^{15}$	acceptors	$8x10^{11}$
706-14.3	$5.0x10^{14}$	acceptors	$5x10^{11}$
707-13.5	$3.5x10^{14}$	acceptors	$7x10^{12}$
710- 9.5	$5.0x10^{14}$	donors	$6x10^{13}$

Detector Performance

Ge:Be photoconductors which have been evaluated are identified in Table I. Detectors measured 1 x 1 x 3 mm^3 with boron implanted contacts ($10^{14}cm^{-2}$ at 25 keV and 2 x $10^{14}cm^{-2}$ at 50 keV) on opposite 1 x 3 mm^2 faces[7]. Layers of titanium (~ 550 Å) and gold (~ 8500 Å) were deposited by argon sputtering. After metallization, the detectors were heated to ~ 300° C for one hour in argon to anneal damage from the implant, activate the boron dopant, and relieve stress in the metal layers. The detector surfaces were polished etched (4:1 HNO_3:HF). Detectors were soldered with pure indium to a 1 mm diameter carbon steel shaft and mounted in polished brass integrating cavities with 1 mm diameter apertures.

The conditions under which the photoconductors were evaluated are summarized in Fig. 2. The low background condition for detector testing is achieved with a combination of reduced filter transmission and the geometric factor imposed by the size of the apertures. An external chopper switches the infrared source between room temperature and liquid nitrogen temperature blackbodies, and the signal is then filtered using a cooled narrow band filter train centered at 42 μm. Calculation of diffraction losses[8] for the limiting aperture (Ø = 1 mm) indicates that the loss for this geometry at 42 μm is approximately 8%. The value given in Fig. 2 for the background limited NEP assumes an $\eta_{responsive} = 1$ in the integrating cavity. A standard transimpedance amplifier was used to measure the detector photocurrent under constant bias voltage[9].

Optimum detector results for several Ge:Be detectors operated at a chopping frequency of 20 Hz are presented in Table II. Results obtained from a Ge:Ga detector ([Ga] = 2 x $10^{14}cm^{-3}$, $[N_D] = 1 \times 10^{12}cm^{-3}$) under the same

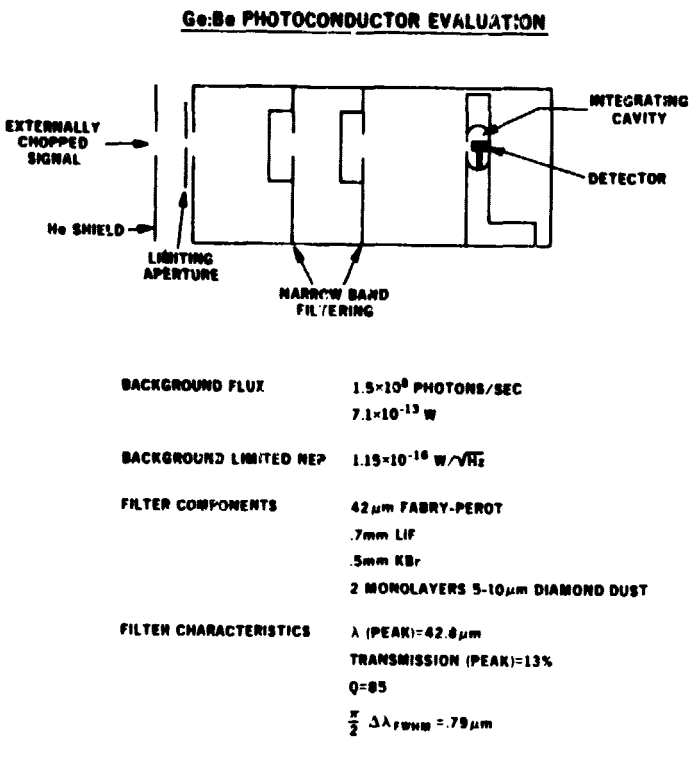

Fig. 2. Ge:Be photoconductor evaluation conditions at 42 μm.

conditions at 42 μm are presented for comparison. These results indicate that Ge:Be detectors can provide higher responsivity and lower NEP than the state-of-the-art Ge:Ga detectors currently used in the 30 - 50 μm range.

Our results support the conclusion of both Bratt et al[3] and Brunsmann et al[4] that the optimum beryllium concentration lies in the range of 5 x 10^{14} to 1 x 10^{15} cm^{-3}. Variations of the beryllium concentration within this range are less critical to the detector behavior than variations which may occur in the concentrations of shallow donors and acceptors. The tabulated data indicates that the responsivity can decrease by over an order of magnitude when the detector operating temperature is reduced from 4.2 to 3.0 K. This temperature dependence can be understood in terms of the carrier lifetime dependence on the temperature-sensitive process of recombination at ionized shallow acceptor sites[10,11]. The responsivity and NEP as a function of temperature for three detectors (operated at constant bias)

TABLE II. Detector Performance at 42 μm.

Detector	Temperature (K)	Applied Field (V/cm)	Responsivity (A/W)	Responsivity ($\frac{\text{carriers}}{\text{photon}}$)	NEP ($W/\sqrt{Hz}$)	$\eta_{\text{detective}}$
Ge:Be 703- 4.2	3.8	10.0	3.7	.11	1.7×10^{-16}	.46
Ge:Be 707-13.5	3.8	3.0	5.1	.15	1.9×10^{-16}	.37
Ge:Be 706-14.3	4.2	5.0	32	.95	2.3×10^{-16}	.25
	3.8	5.0	6.4	.19	1.9×10^{-16}	.37
	3.0	5.0	0.76	.022	2.6×10^{-16}	.19
	3.0	9.0	1.6	.047	2.2×10^{-16}	.27
Ge:Ga	3.0	2.5	1.0	.029	3.0×10^{-16}	.15

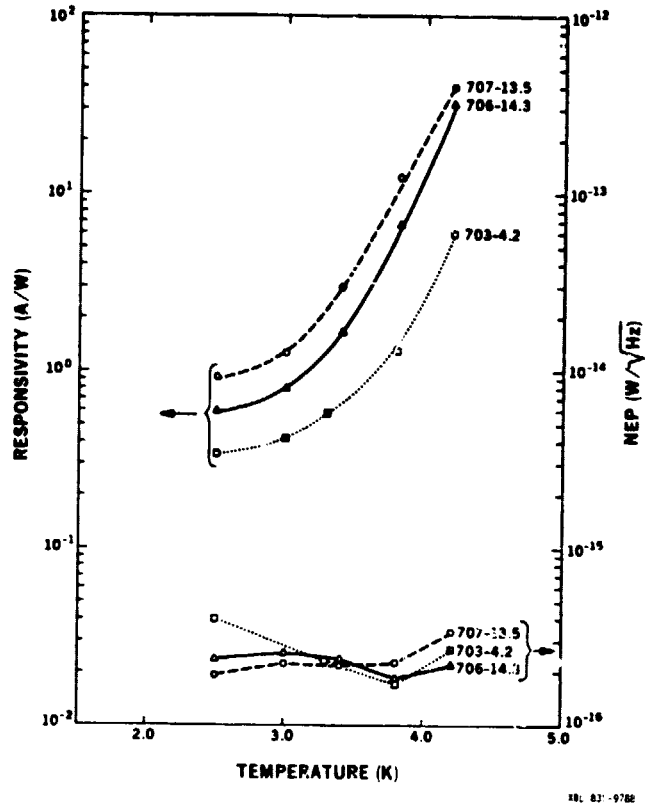

Fig. 3. Responsivity and NEP as a function of temperature for Ge:Be detectors 703-4.2, 706-14.3, and 707-13.5 at a constant field of 5.0 V/cm and a chopping frequency of 20 Hz.

are presented in Fig. 3. Minimum NEP is attained at 3.8 K, although higher responsivity can be obtained if necessary at 4.2 K without a major decrease in the signal-to-noise ratio. The increase in responsivity with decreasing beryllium concentration indicates that the concentration of ionized sites due to compensation is not the sole factor in determining the mobility and that scattering due to neutral beryllium is significant at these concentrations and temperatures.

In Figure 4, the responsivity as a function of temperature at constant bias for detector 710-9.5 [$N_{D(shallow)} > N_{A(shallow)}$] is compared to that of detector 706-14.3, a device with the same beryllium concentration. As the theoretical models would predict, overcompensation of the shallow acceptors which leads to significant compensation of the beryllium severely reduces the mobility and eliminates the strong temperature dependence of the lifetime which is

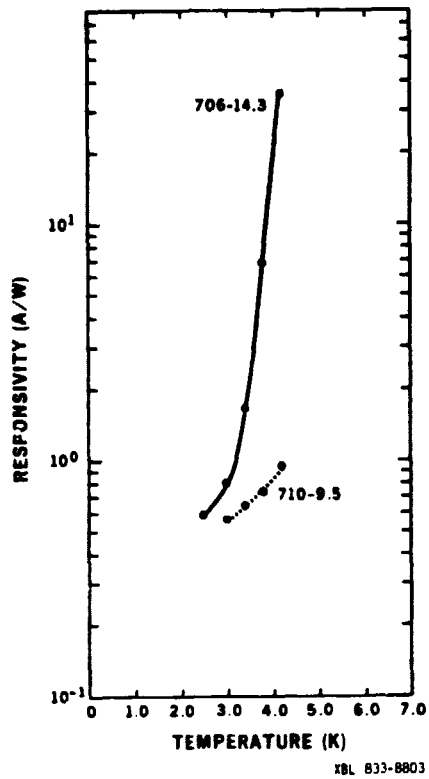

Fig. 4. Responsivity as a function of temperature for Ge:Be detectors 706-14.3 and 710-9.5 at a constant field of 5.0 V/cm and a chopping frequency of 20 Hz.

present when the ratio $N_{D(shallow)}/N_{A(shallow)}$ is closer to unity. In a case where $N_{A(shallow)} >> N_{D(shallow)}$, a similar effect would be expected. Thus, the high values of the responsivity (G_n = .95 carriers/photon) can only be attained when good control can be exercised over the residual impurity concentration in the detector material.

Ge:Be detectors are significantly less affected by the current spiking behavior which is common in Ge:Ga devices. Detectors operated at 3.8 and 4.2 K do not display any spiking behavior throughout the operating bias range. At 3.0 K, spiking occurs only very close to the breakdown field and does not extend to lower biases where the optimum NEP is attained.

Summary and Conclusions

Ge:Be photoconductors produced from Czochralski-grown single crystals provide higher responsivities and lower NEP

than the Ge:Ga detectors currently used in the 30 - 50 μm region. Consistent detector performance has been obtained with material selected from three different crystals and from detectors which were fabricated from different regions of a single crystal slice. These prototype Ge:Be detectors are very stable devices. Performance approaches the photon noise limit to within a factor of 1.4 ($\eta_{detective}$ = 46%).

The temperature dependence of the responsivity is strongly influenced by both the absolute concentration and the concentration ratio of shallow donors and shallow acceptors. The control of these shallow levels which can be attained down to the $10^{10} cm^{-3}$ range with a special Czochralski crystal puller offers interesting possibilities for the optimization of Ge:Be detectors. Precise compensation of shallow residual acceptors should lead to a detector with very high responsivity at 4.2 K. Finally, the insensitivity of the NEP over the 3.0 - 4.2 K temperature range indicates that Ge:Be detectors could easily be integrated with other devices which are more restricted in their optimum operating temperature range.

Acknowledgments

We are indebted to P. L. Richards and M. R. Hueschen for their advice in the design of the photoconductor test facility. D. Watson of C. H. Townes' group fabricated and characterized the filters. W. L. Hansen prepared the master alloy.

This work was supported by NASA Contract No. W-14,606 under Interagency Agreement with the Director's Office of Energy Research, Office of Health and Environmental Research, U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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