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Ge:Be FAR INFRARED PHOTOCONDUCTORS

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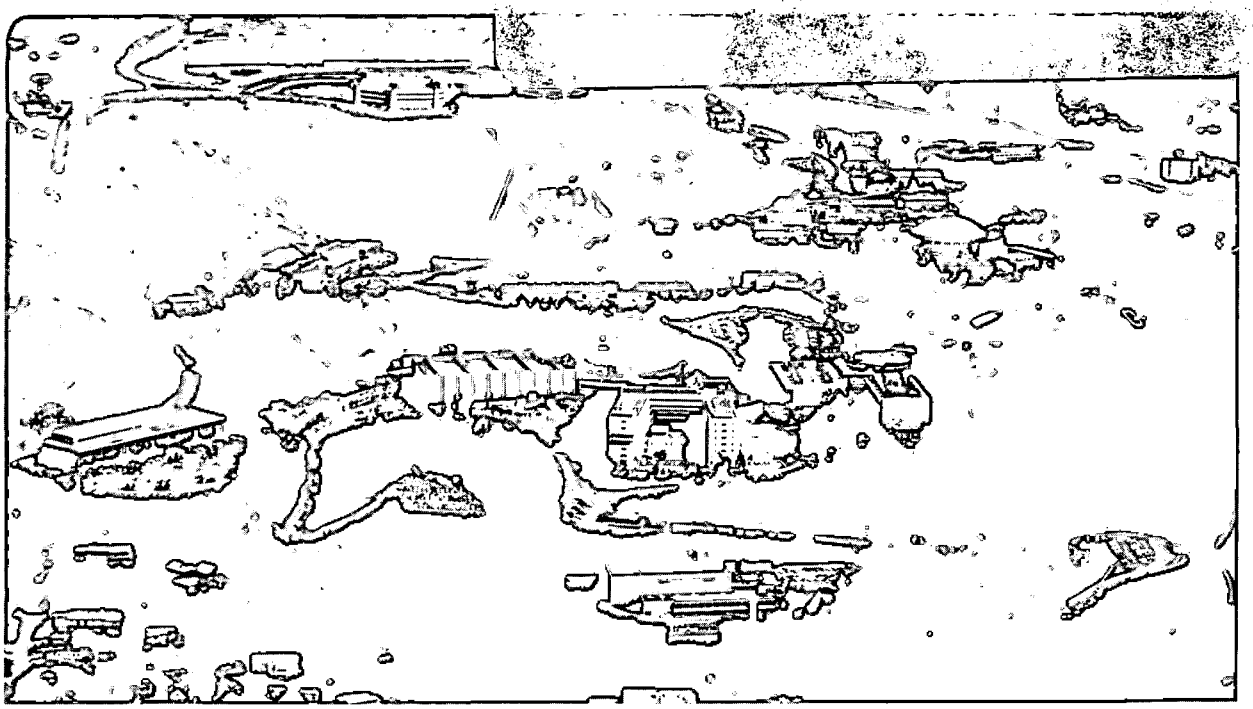

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Ge:Be Far Infrared Photoconductors

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Abstract

Ge:Be photoconductors have been optimized for the 30-50 μm wavelength range. Crystal growth of detector quality material requires good control of both the Be and residual impurity doping. Detective quantum efficiencies of η_d = 46% at 5 A/W have been achieved at a photon background of 10^8 p/s. The responsivity of Ge:Be detectors can be strongly temperature-dependent when the residual shallow levels in the material are closely compensated. Transient responses on the order of ~1 second have been observed in some materials. The role of residual shallow impurities on the performance of photoconductors doped with semi-deep and deep impurities is discussed.

Introduction

Recent development of Ge:Be photoconductor material and devices has led to the availability of optimized detectors for the 30-50 μm wavelength range. This paper will review the crystal growth, characterization, and detector performance of this material. The temperature dependence and transient behavior will be examined to illustrate some of the remaining issues concerning device behavior. Finally, a general summary of criteria for selecting multi-level material for detectors such as Ge:Be, Si:Ga, or Si:In will be presented.

Investigation of the photoconductive response of Ge:Be was first reported in 1967 (1). Be is a double acceptor in Ge and is the shallowest of the helium-like, group II impurities. Its ionization energies are 24.8 and 58 meV, corresponding to wavelength thresholds of 50 and 21 μm (2). In addition, its high solubility in the Ge lattice (3) makes it especially suitable as a dopant for an extrinsic photoconductor. A schematic response for Ge:Be is presented in Figure 1 which shows that Ge:Be photoconductors should be useful for attaining high sensitivity in the wavelength gap between the shallow levels in Si and the peak response of Ge:Ga.

Ge:Be Crystal Growth

Despite early encouraging results, however, the difficulties associated with the growth of Ge:Be have, until recently, prevented these detectors from being fully developed and utilized. Be forms a very stable oxide and can react with oxygen present in either the silica crucible or the ambient gas in the crystal puller. The oxygen content of the melt environment, therefore, is a critical factor in determining whether Be will precipitate as stable and neutral BeO or remain as an isolated dopant which is electrically active in a substitutional site.

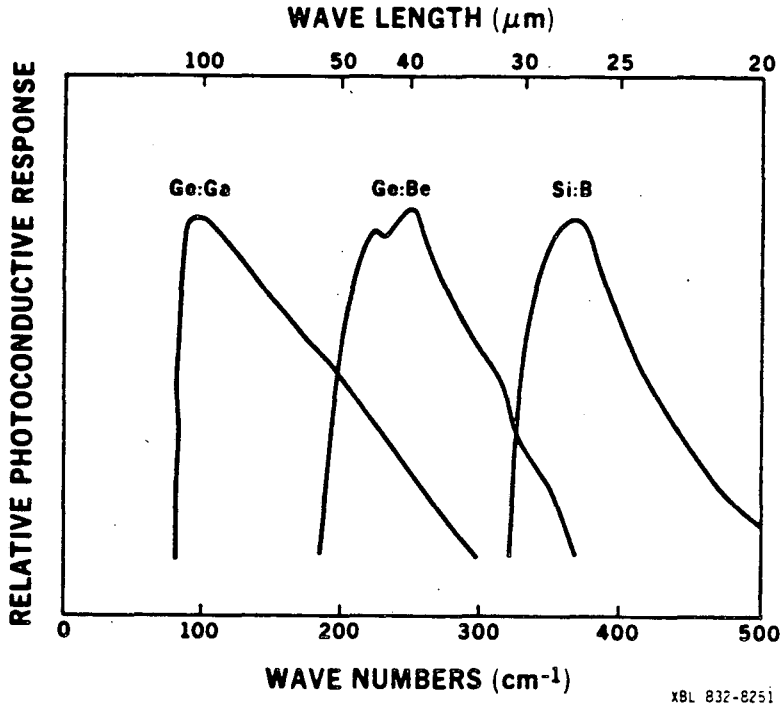


Figure 1
Schematic photoconductive response for Ge:Be

Thermodynamics calculations, based on free energy of formation data and the mass action law, can give an indication of the stability of an oxide under various conditions of temperature, concentration in the melt, and environment. Calculations done following the method used by Darken (4) indicate that stable BeO would be expected to form in equilibrium under a H_2 atmosphere when p_{H_2O}/p_{H_2} exceeds 5.5×10^{-7} for crystal growth at 1200 K with a Be concentration in the melt of 5×10^{15} cm^{-3} (5). Since the usual ratio of p_{H_2O}/p_{H_2} partial pressures attained during crystal growth is approximately 10^{-5}, the H_2 atmosphere commonly used for high-purity growth is unsuitable for growing Be-doped crystals since the formation of BeO is thermodynamically favorable. In addition, BeO is more stable, on a relative scale, than the SiO_2 which composes a silica crucible. This suggests that Be in the melt would react with a SiO_2 crucible within the limits imposed by diffusion and convection.

Thermodynamic conditions, therefore, dictate that Ge:Be be grown in a less oxygen rich environment. We have achieved reliable and reproducible Be doping using Czochralski growth from a carbon susceptor under high vacuum (10^{-6}-10^{-7} torr). Czochralski growth provides good control of residual impurities and results in low dislocation densities (< 1000 cm^{-2}) in the single crystal material (6). Doping of the melt is achieved by using a heavily doped master alloy. Use of a master alloy provides a more controlled method of doping than the direct addition of pure Be. The weight of the dopant can be determined more precisely, and a Hall effect measurement can be used to reliably determine the Be concentration in the master alloy.

Seven Ge:Be crystal have been grown for photoconductor material, both to study the effects of shallow level doping and to develop a supply of material for use in providing optimized detectors for various operating conditions. These crystals are summarized in Table 1. Optimum Be doping for maximum absorption without excessive hopping conductivity ranges from 5×10^{14} cm^{-3} to 1×10^{15} cm^{-3} depending on the residual donor concentration.

TABLE 1.

Crystal	[Be] (cm^{-3}) Seed End	Shallow Level Characterization	Growth Conditions
703	10^{15}	$N_A > N_D$	carbon susceptor, vacuum
706	5×10^{14}	$N_A > N_D$	carbon susceptor, vacuum
707	10^{14}	$N_A > N_D$	carbon susceptor, vacuum
710	5×10^{14}	$N_D > N_A$	carbon susceptor, vacuum
719	4×10^{14}	Variable	carbon susceptor, H_2
727	6×10^{14}	$N_A > N_D$	carbon susceptor, vacuum
728	10^{15}	Variable	carbon susceptor, H_2

Material Characterization

Schematic band diagrams for Si:In and Ge:Be (showing only the first ionization stage for Ge:Be) are given in Figure 2. Ge:Be, as well as Ge:Hg, Ge:Zn, Si:Ga, Si:In, etc., can be referred to as "multi-level systems" because there will be additional shallow levels (B in Si, B and Al in Ge) present in the bandgap which will affect the photoconductor performance. Variable temperature Hall effect and resistivity measurements are necessary to determine the concentration and compensation of the residual shallow levels in such materials (7).

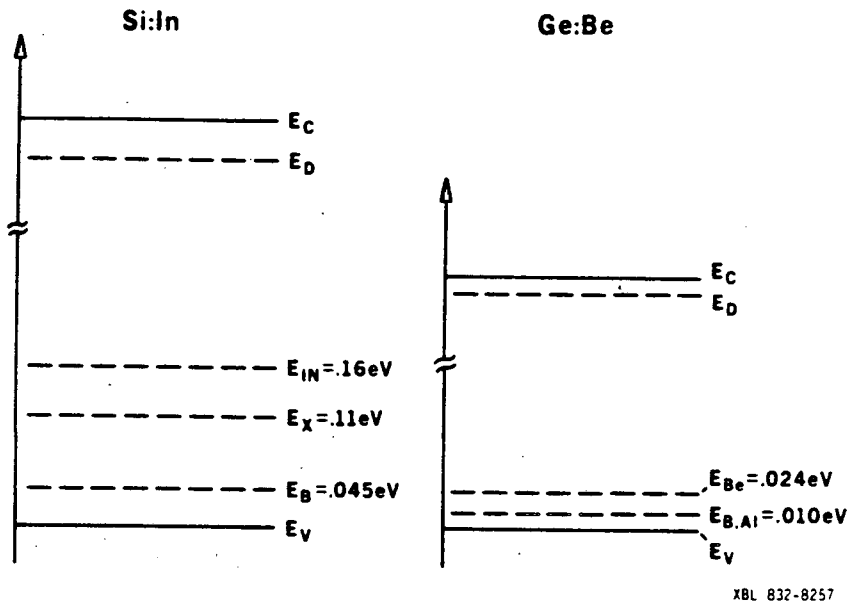


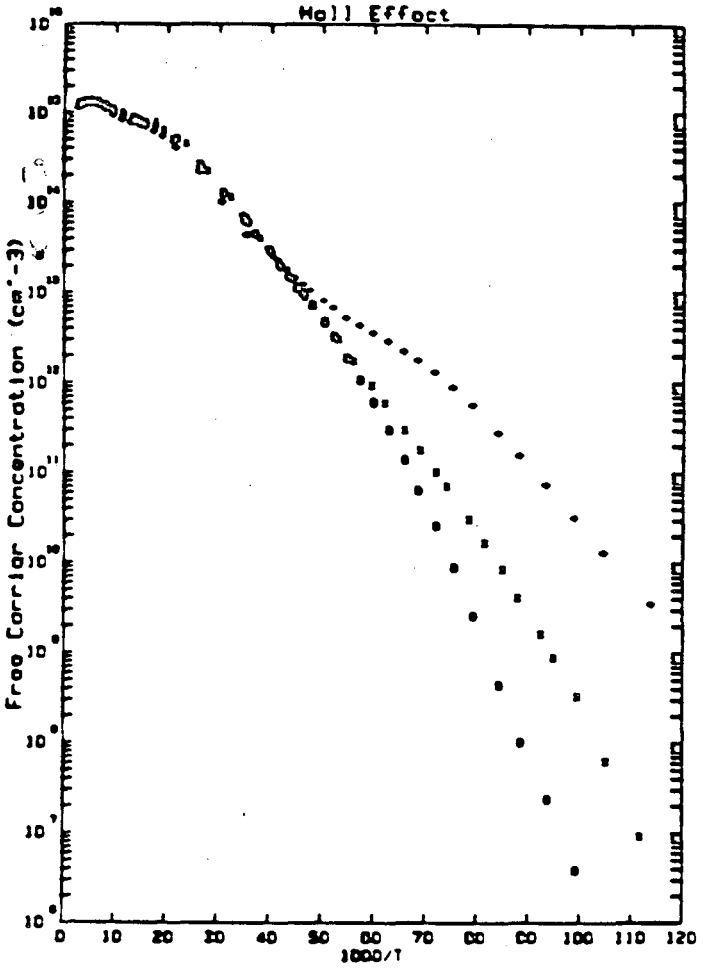
Figure 2
Schematic band diagrams for Si:In and Ge:Be indicating the presence of residual shallow acceptors

The free carrier concentration as a function of inverse temperature and the corresponding resistivity data are plotted in Figure 3 for a number of Ge:Be samples with varying compensation and concentration of residual shallow impurities. The experimental techniques for controlling these residual shallow levels will be discussed in a later section.

Detector Performance

Ge:Be detectors have been evaluated for responsivity and NEP as a function of bias and temperature at a background flux of 1.5×10^8 photons/sec (8). Narrow-band filters, consisting of Fabry-Perot and restrahlen salt filters (9), were used to restrict the photon energy to within ± 1 μm of 42 μm, and the detectors were tested in brass integrating cavities. Results are summarized in Figures 4 and 5. The comparison to Ge:Ga was performed with each detector operating at its optimum temperature, as determined by optimum signal to noise ratio.

The best result obtained to date for Ge:Be detectors is a detective quantum efficiency $((NEP_{exp}/NEP_{blip})^2)$ of 46% with a responsivity of 5 A/W. One sees from Figure 4 that the value of NEP does not vary greatly for the different materials tested, except at the lower bias where Johnson noise of the feedback resistor becomes significant. Under these conditions, highest responsivity will result in lowest measured NEP. The difference in responsivity in the various materials is due to the difference in free carrier mobility resulting from differences in Be concentration.



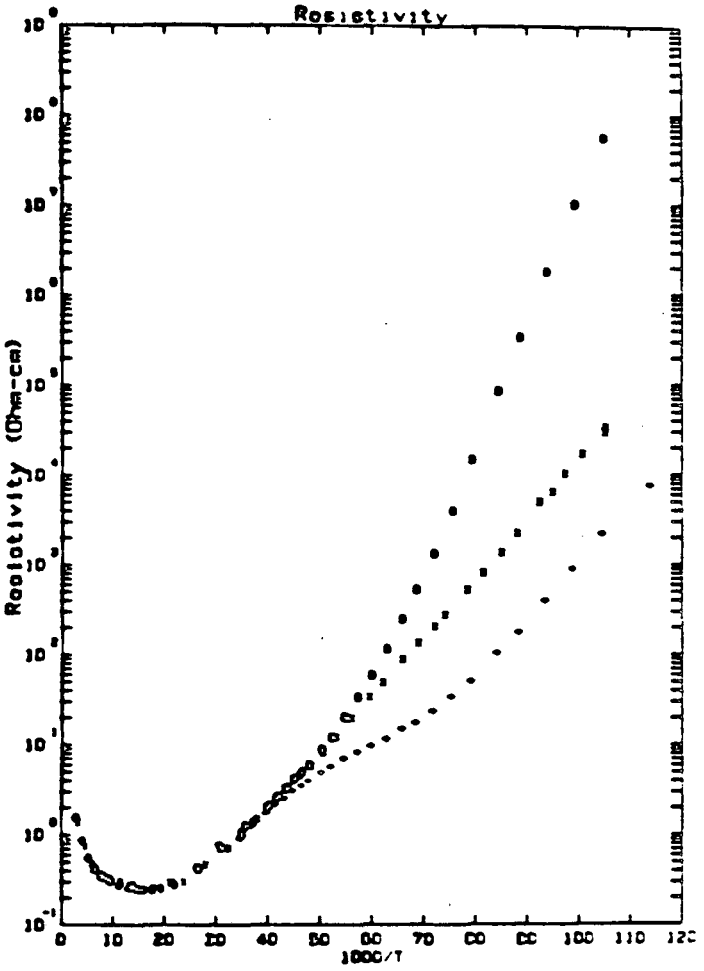


Figure 3

Free hole concentration and resistivity as a function of inverse temperature for the following Ge:Be materials:

+ Ge:Be 728-4.3 As grown
x Ge:Be 728-4.3 Annealed 75 minutes/600°C
□ Ge:Be 728-4.3 Annealed 90 minutes/660°C

Note the increase in resistivity of the fully annealed material.

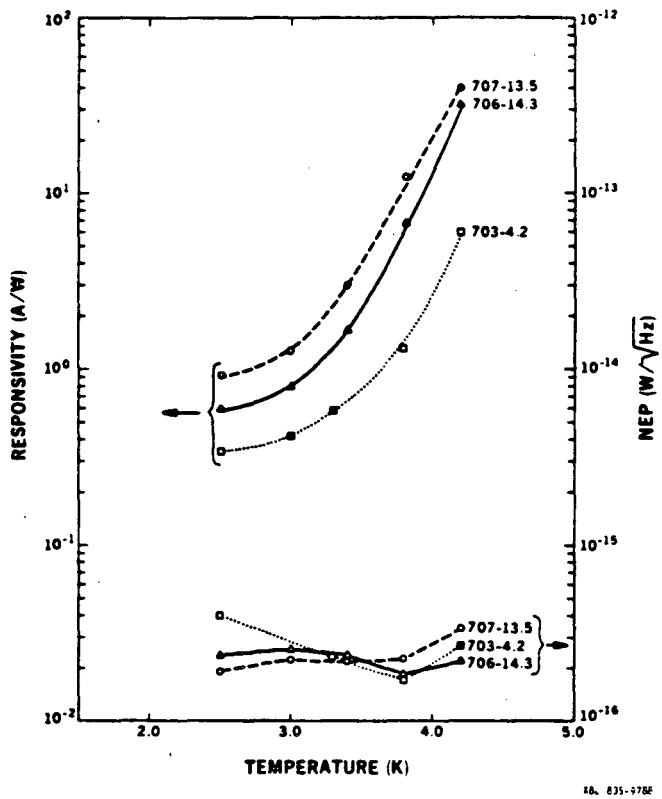


Figure 4
Responsivity and NEP versus temperature for three Ge:Be detectors
$NEP_{back.lim.} = 1.2 \times 10^{-16}\ W/\sqrt{Hz}$

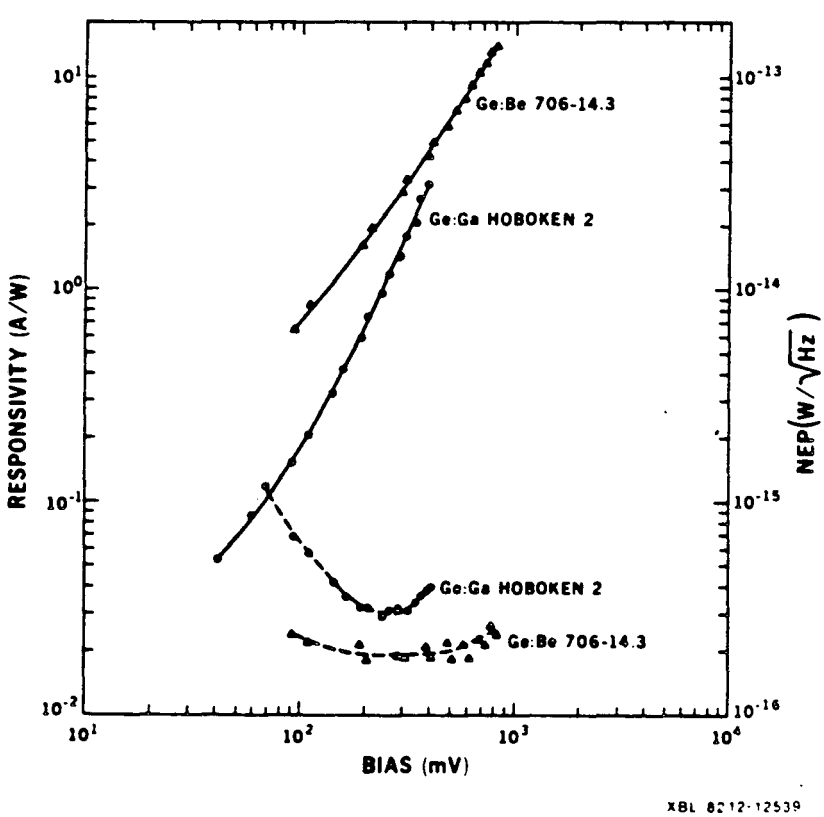


Figure 5
Responsivity and NEP as a function of bias for a Ge:Ga and Ge:Be detector under the same test conditions
T(Ge:Ga) = 3.0 K; T(Ge:Be) = 3.8 K; $NEP_{back.lim.} = 1.2 \times 10^{-16}\ W/\sqrt{Hz}$

The improved performance of the LBL Ge:Be as compared to Ge:Ga has been confirmed in the use of these detectors in aircraft-based astronomy. These detectors have been flown on the Kuiper Observatory in a far-infrared grating spectrometer (J. Houck et.al., Cornell University (10)). They report an inprovement of a factor of 2-3 in NEP over the Ge:Ga that was previously used to cover the Ge:Be wavelength range.

Temperature Dependence of Responsivity

The data in Figure 4 indicate that the responsivity of Ge:Be can be strongly temperature dependent. The responsivity increases over an order of magnitude as the device temperature is raised from 2.5 to 4.2 K. A responsivity increase, under fixed bias for a given intercontact length L, must be due to either an increase in free carrier mobility or lifetime. This temperature dependence, however, is much stronger than would be predicted based on the temperature dependence of the lifetime as given by the cascade capture model (11,12) or the well characterized scattering mechanisms that determine mobility (13).

Such strong increases in detector responsivity with increasing temperature have been predicted for the case of multi-level semiconductors in which the shallow acceptors are closely compensated, i.e., $N_{A(shallow)} \approx N_D$ (14,15). An increase in free carrier lifetime can occur when thermal ionization from the shallow levels becomes strong enough that these centers no longer act as effective recombination centers. The temperature at which this increase in lifetime will occur is given approximately by:

$$T_c = \frac{E_A}{k \ln(\frac{Nv}{gp})}$$

where E_A is the activation energy of the shallow level dopant, p is the free hole concentration, N_v is the valence band density of states, g is the degeneracy factor, and k is Boltzmann's constant.

The models predict however, that the maximum responsivity which can be obtained is strongly dependent on the exact compensation of the shallow residual impurities, and that variations of 5-10% in the quantity $[N_A-N_D]$ are sufficient to change the maximum responsivity by over an order of magnitude. For this reason. special attention must be given to ways to achieve very close compensation of residual levels if this enhanced responsivity is to be achieved consistently and reproducibly in a large number of devices.

One way of obtaining close compensation of shallow levels is to use a high purity crystal growth facility and, if necessary, to counterdope, generally with the n-type impurity. In Ge, residual impurities can be controlled to levels of $\sim 10^{10}$ cm^{-3} under optimum growth conditions (6), while high purity Si generally has [B] and [P] $\sim 10^{13}$ cm^{-3}. The high responsivity values shown for the Ge:Be detectors in Figure 5 were all attained in crystals in the as-grown condition, without intentional counter-doping.

A second approach, which has been used to achieve close compensation in Si, is neutron transmutation doping (16). NTD is used to provide uniform doping (Si→P) and can be done in a controlled manner since the concentration of P produced is directly proportional to the fluence of thermal neutrons to which the sample is exposed. This technique could also be used in Ge although the process would be less efficient since the transmutation of Ge leads to the production of both donors and acceptors with a fixed compensation ratio of $N_D/N_A \sim 0.4$ (17).

A third method, which is presently being evaluted as a means of obtaining closely compensated material, is to control the concentration of hydrogen-related impurity complexes such as A(Be-H) and A(Zn-H) (18,19). These shallow acceptors, which are present in the as-grown state of crystal grown under a H_2 atmosphere, can be removed with thermal annealing at temperatures of 500-700°C. The effect of this is seen in the Hall effect data of Figure 3 where different annealing treatments were used to obtain a variety of degrees of compensation of the shallow levels. With the proper choice of annealing treatment, very close compensation of the shallow levels can be achieved. Evaluation of photoconductors made from these various materials is in progress.

Transient Response of Ge:Be Photoconductors

In an idealized photoconductor model, neglecting all space charge and contact-related effects, the transient response of the device will be limited by the free carrier lifetime, which is generally on the order of 10^{-9} to 10^{-6} sec for Ge detectors at low temperatures. Other models, supported by extensive experimental data, also show that, for large photoconductive gain and high electric fields, detector response can be limited by the dielectric relaxation of space charge regions near the contact which are created by initial sweep-out conditions (20,21). In practice, however, some very long time constants, on the order of seconds, are observed to characterize some fraction of the total photoconductive response in many detectors. Usually this is a very small part of the total signal and the ac and dc responsivities do not vary greatly for frequenices less than the dielectric relaxation frequency.

In the Ge:Be detectors, however, as well as in the Ge:Zn detectors, we have observed time constants on the order of seconds, where the slow component of the signal is up to 10 times greater in magnitude than the initial fast component. This is illustrated in Figure 6 for a Ge:Be detector as a function of increasing temperature for a fixed bias. The data has been compiled schmatically in Figure 7 to show how the absolute and relative magnitude of the slow component increases with increasing device temperature.

Several experiments have clearly demonstrated that this slow component is not a dielectric-relaxation time controlled behavior. First, the dielectric relaxation time constant, $\rho\epsilon\epsilon_0$, can be calculated directly from the measured detector resistance and is found to be on the order of 1-10 msec. This is two to three orders of magnitude faster than the time constant of the observed behavior. Secondly, the time constant of the slow response is temperature-dependent, but is not affected by photon-induced changes in background free hole concentration, i.e., it is not dependent on material resistivity. Finally,

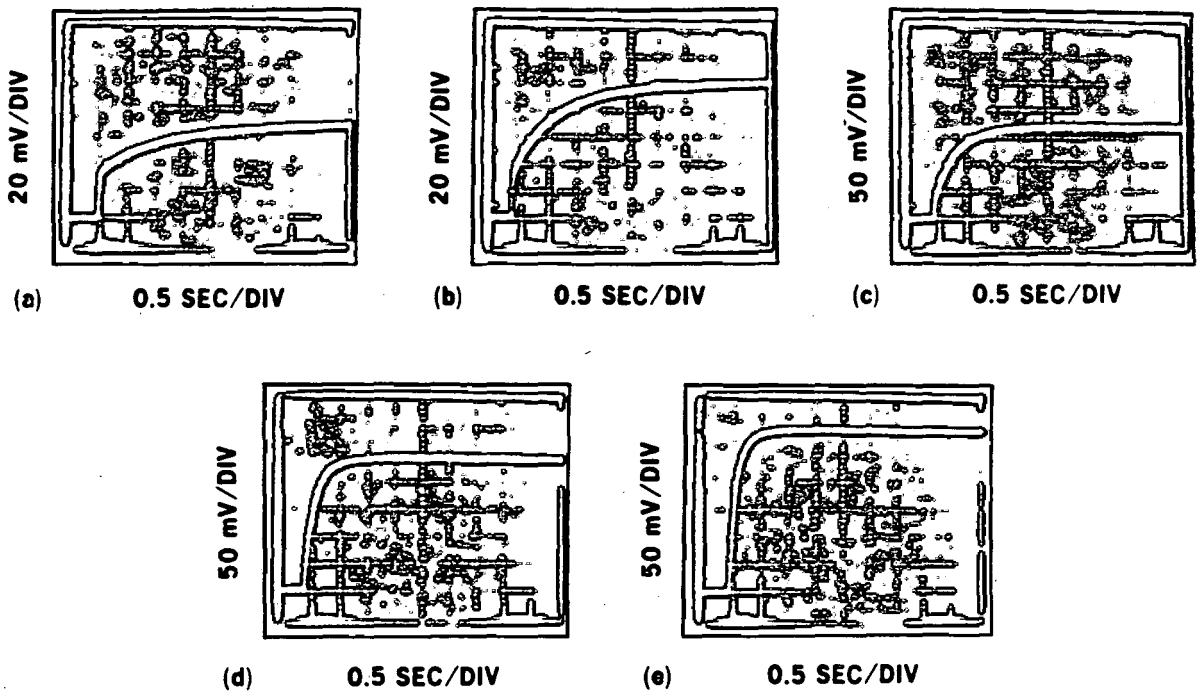


Figure 6
Photoconductive response as a function of time for a Ge:Be detector showing a slow time constant dominated response.
a) 2.5 K b) 2.6 K c) 2.7 K d) 2.8 K e) 2.9 K

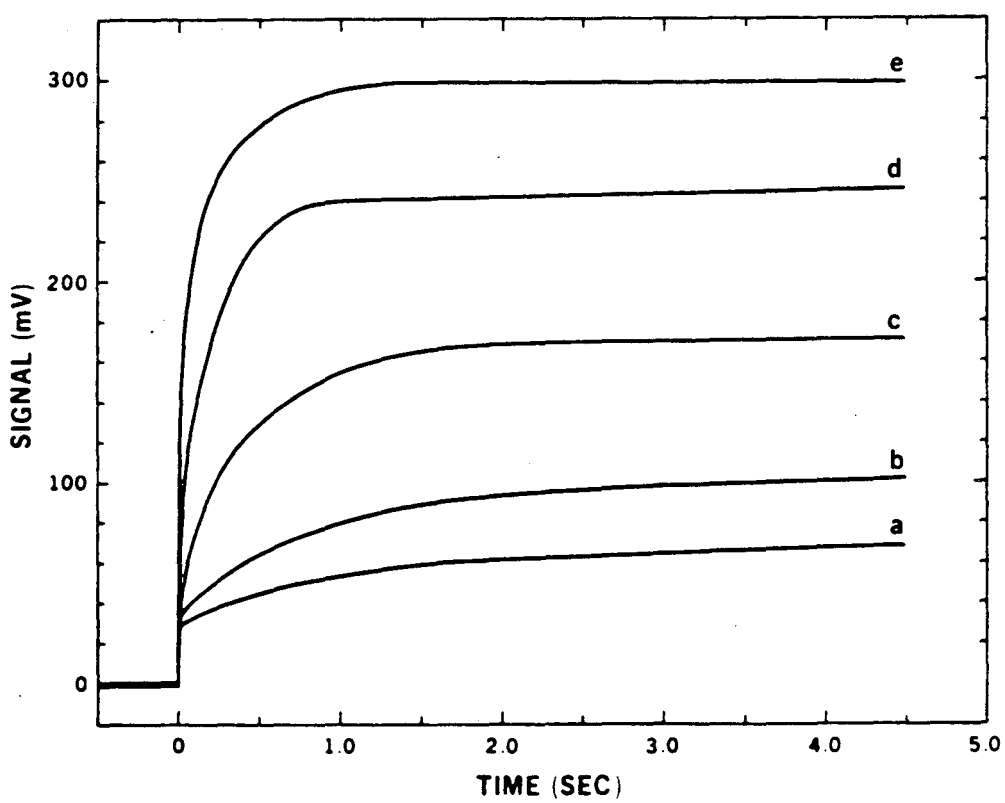


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Figure 7
Data from Figure 6 compiled on a constant vertical axis
a) 2.5 K b) 2.6 K c) 2.7 K d) 2.8 K e) 2.9 K

the fast component of the signal does not saturate with increasing field as one would expect for dielectric relaxation.

From this evidence, we conclude that the slow transient response we observe is not explained by any of the present models for transient phenomena in photoconductors. We believe that the slow response may be associated with changes in the electric field profile inside the device due to slow changes in the space charge distribution in the near-contact region. In this region, free holes from the implanted contact diffuse into the bulk material. They are trapped by ionized acceptors and create a space charge region which determines the near-contact profile of the electric field. Steady state solutions for a theoretical model which includes the effects of contacts and space charge have recently been published (22). Progress has been made on the solution of the time-dependent response and the results from this model will be compared to the Ge:Be experimental results (23).

Material Selection for Multi-level Photoconductors

Because of the large role that residual shallow levels play in determining the performance of a multi-level photoconductor, the selection of optimized material for detectors such as Ge:Be or Si:Ga requires full characterization of the material with regard to both primary and residual dopants. In addition to the standard compromises (speed versus responsivity, high α versus hopping conduction, etc.) one must also determine, based on the temperature of device operation and the background flux levels expected during observation, whether enhanced responsivity due to close compensation is a desirable goal. An attempt has been made in Table 2 to consider the factors involved in material selection of multi-level materials.

One sees that the shallow levels will determine both the responsivity and the thermally generated current which will be present in the absence of a photon flux ("dark current"). Routine crystal growth, without counterdoping or NTD, will generally lead to the case $N_{A(shallow)}>N_D$ in both Si and Ge. This is usually undesirable with regard to both responsivity and dark current for the case of very low background astronomy. In compensated material, very high resistivity values can be obtained (see Fig. 3). A combination of materials characterization and dark current measurements on actual devices will be required to determine if observed dark currents at low temperature are material related or due to other effects such as surface leakage.

Finally, an example will illustrate the use of Table 2. Consider a Si:In photoconductor being developed for a low background ($p \sim 10^8$ p/s) space application on a focal plane at T=3.0 K. It is generally true that float-zone Si (the technique used to produce Si:In) has a net shallow acceptor concentration due to the presence of residual boron. Boron is hard to remove from silicon because it has a segregation coefficient very close to one. Perhaps, because of the low background and small signals, one desires to have as high a responsivity as possible in order to overcome some fixed level of background noise, such as electronics related noise. Finally, suppose the resistivity in the as-grown case is sufficiently high at 3.0 K to eliminate measurable dark current noise.

TABLE 2

Material Selection:
Shallow Level Compensation

$N_D \gg N_{As}$	$N_D > N_{As}$	$N_{As} > N_D$	$N_{As} \gg N_D$
Highest ρ	High ρ	Lower ρ	Lowest ρ
Lowest dark current	Low dark current	Higher dark current	High dark current
$R \propto \frac{1}{N_D}$	$R \propto \frac{1}{N_D}$ for $T < T_c$		$R \propto \frac{1}{N_D + p}$

$$R \propto \exp(-E_B/kT) \text{ for } T > T_c$$

$$\text{where } T_c = \frac{E_A}{k \ln(\frac{Nv}{gp})}$$

To determine if one should counterdope (i.e., add donors) to attempt to achieve $N_A \sim N_D$, one should calculate the temperature at which the lifetime increase due to exact compensation will occur. In this case, for $p = \dot{p}\tau = 10^3$ cm^{-3} and E=45 meV for B, T_c= 17 K. Thus, the focal plane temperature is so far below T_c that the responsivity will be given by

$$R \sim 1/N_D$$

and the addition of counterdopants would be detrimental rather than beneficial to achieving high responsivity. If, however, the resisitivity of the as-grown material was not high enough to eliminate dark current effects, then counterdoping would be required, with some sacrifice in responsivity. Analysis of similar cases in Ge might lead to other conclusions because the shallower levels in Ge means that enhanced responsivity can be achieved at lower temperature for a given flux.

Conclusions

The performance of Ge:Be in the 30-50 μm wavelength range has been reviewed and shown to be superior to the Ge:Ga detectors which have previously been used in this application. The use of Czochralski growth from a carbon susceptor under high vacuum has been effective in achieving reliable crystal growth and in avoiding the precipitation of Be as stable BeO.

Shallow residual impurities are present in all extrinsic photoconductors based on semi-deep and deep levels (Ge:Be, Ge:Hg, Si:Ga, Si:In) and affect both the resistivity and responsivity of the devices. Enhanced responsivity can be attained in these materials if the shallow levels are closely compensated and the device is operated at sufficiently high temperature. Choices of optimized material for detectors will depend on the resistivity and responsivity required for a particular astronomy application.

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