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MASTER

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DEVELOPMENT OF HIGH RESPONSIVITY Ge:Ga PHOTOCONDUCTORS*

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Abstract

Czochralski-grown gallium-doped germanium (Ge:Ga) single crystal samples with a compensation of 10^{-4} have been modified by the indiffusion of Cu to produce photoconductors which provide NEPs comparable to current optimum Ge:Ga detectors, but exhibit responsivities a factor of 5-6 times higher when tested at a background photon flux of 10^8 photons/sec at λ=93 μm. The introduction of Cu, a triple acceptor in Ge which acts as a neutral scattering center, reduces carrier mobility and extends the breakdown field significantly in this ultra-low compensation material.

Introduction

The use of far-infrared photoconductors under conditions of very low photon flux has placed new demands on device performance and sensitivity. Such flux levels are encountered, for example, in astronomical observation from spaceborn instruments or in experiments utilizing very narrow band filters. Under such conditions, Johnson or amplifier noise may be a significant noise source, and the best performance is obtained by using high responsivity detectors.

Doped semiconductor detectors, generally referred to as extrinsic or impurity photoconductors, are used as sensitive infrared detectors over a wide wavelength range (2-200 μm for Si and Ge)(1). Gallium-doped germanium (Ge:Ga), with a long wavelength cut-off of 120 μm, is the best developed and most common detector for low background applications for wavelengths longer than 50 μm. Recent work on the characterization of photoconductors produced from single crystal Ge:Ga with ultra-low compensation ($K=10^{-4}$, i.e. minority impurity (donor) concentration $N_D=2\times10^{10}cm^{-3}$ for a majority (acceptor) concentration $[N_{Ga}]=2\times10^{14}cm^{-3}$) has shown that long lifetimes ($\tau=10^{-7}-10^{-5}$sec) and high mobilities ($\mu=8\times10^5cm^2V^{-1}s^{-1}$) are attained in this material, leading to photoconductors with very high responsivities.(2) Material with such low compensating donor concentrations is now available due to the use of high purity Ge crystal growth facilities for the growth of doped photoconductor material.(3) The long lifetimes and high mobilities are both due to the reduction in the number of ionized centers in the material. The increase in mobility in low compensation material is ultimately limited by neutral impurity scattering. Under low photon background conditions, however, the lifetime increases can be very large since the lifetime is inversely proportional to the ionized acceptor concentration (N_A^-), and $N_A^- = N_D$ for $Q\sigma N_A\tau << N_D$, where Q = background flux, σ = photoionization cross section and N_A = neutral acceptor concentration.

The performance of the low compensation material as detector material has been limited in practice by the lower maximum dc operating bias which accompanies the increases in lifetime and mobility. Free carriers can pick up energy at a greater rate from the electric field and so attain the average energy required for impact ionization at a lower applied field. The average breakdown field due to impact ionization for standard Ge:Ga detectors ($[Ga]=2x10^{14}cm^{-3}, K\sim10^{-2}$) is 3-4 Vcm^{-1}, while low compensation detectors begin to undergo impact ionization at ~1 Vcm^{-1}. The best responsivity that can be achieved therefore in the low compensation material is not significantly higher than that achieved in standard material at a higher applied field. In addition, the noise and spiking levels are often unacceptably high in a bias range well below the breakdown bias.

By reducing carrier mobility through the introduction of neutral scattering centers, the onset of breakdown, as indicated by the presence of large noise spikes just prior to a dramatic increase in dc current, can be extended to higher applied field. Cu, a triple acceptor in a substitutional position, was selected as a neutral scattering species because it can be easily introduced by diffusion and because the ionization energy (4) of the first hole (E_v+ 43.2meV) is large enough to assure that thermal and optical generation from this level (assuming appropriate filtering) is negligible at the optimum operating temperature (≈3.0 K) for Ge:Ga detectors.

Experimental

Several 1mm slices of ultra-low compensation Ge:Ga were Cu plated in an aqueous copper cyanide solution and then heated under Ar gas to 600°C for 1 hr to allow for Cu diffusion throughout the bulk. Slices were then polish etched in a mixture of HNO_3 and HF (5:1) and B implanted ($1x10^{14}$ cm^{-2}, 25 keV; $2x10^{14}$ cm^{-2}, 50 keV) to provide ohmic contacts.(5) Implanted slices were then reheated to 600°C for 15 minutes and quenched directly into ethylene glycol. This heating cycle was designed to dissolve any Cu precipitates that may have formed after the initial diffusion and also to anneal the implanted contact. After quenching, layers of Ti (~550Å) and Au (~8500Å) were deposited by Ar sputtering. The standard thermal annealing step to relieve stress in the metal layers was eliminated in this case to avoid precipitation of the Cu. Experimental studies on the indiffusion of Cu in Ge indicate that a concentration of electrically active Cu of approximately 10^{14} cm^{-3} would be expected to be introduced by quenching from 600°C.(6)

The detectors measured 1x1x3 mm^3 with contacts on opposite 1x3 mm^2 faces. They were soldered with pure indium to a 1 mm diameter carbon steel post and mounted in polished brass integrating cavities with 1 mm diameter apertures. The detectors were evaluated in a specially designed cryostat for low background testing using narrow band filters at 93 μm.(7) Background parameters and filter characteristics are summarized in Table 1.

Table 1. Photoconductor Evaluation Conditions at 93 μm

Background Flux	2.7×10^{7} photons/sec 5.8×10^{-14} W
Background Limited NEP	2.0×10^{-17} $W/\sqrt{Hz}$
Filter Components	93 μm Fabry-Perot .5 mm KCl 1.0 mm BaF_2 2 mil black polyethylene 1 mono-layer 6 - 12 μm diamond dust 7 mg ZnO for a 1.5 cm disk
Filter Characteristics	λ(peak) = 93.2 μm Transmission (peak) = 13.2 % Q = 140 $\frac{\pi}{2}\Delta\lambda_{FWHM}$ = 0.8 μm

Detector Performance

Figure 1 compares detector performance of the low compensation material before and after Cu diffusion. Mobility data from variable temperature Hall effect and resistivity measurements (Figure 2) show the effect of the Cu. Neutral scattering by the Cu reduces the mobility by a factor of approximately three in the range where neutral impurity scattering dominates. This results in a reduction of responsivity by approximately the same factor at low bias, since responsivity is directly proportional to the free carrier mobility. This reduction in responsivity is more than compensated for by the ability to go to higher electric field.

In Figure 3, the Ge:Ga:Cu detector performance is compared to that of a standard state-of-the-art detector. One sees that responsivity values of 30 A/W (0.4 carriers/photon) obtained with the Ge:Ga:Cu detectors are 5-6 times higher than those generally achieved by today's optimum Ge:Ga detectors, while comparable values of NEP are obtained. The NEP of the Ge:Ga:Cu detector becomes amplifier or Johnson noise limited at a significantly lower bias at this fixed background due to the higher photoconductive gain.

The response of the Ge:Ga:Cu detectors to a square wave photon pulse is characterized by multiple time constants including a long bias dependent time constant which can reduce the signal size at 1.25 Hz to 75-97% of its DC value. This time constant is also present in standard Ge:Ga and ultra-low compensation Ge:Ga detectors. It is most pronounced in the ultra-low compensation material where it can reduce the signal size to 55-80%. No evidence of the "pulse hook anomaly"(8) has been observed in the Ge:Ga:Cu detectors. They do show the characteristic spiking behavior close to the breakdown field, but this can be avoided by operating at fields of ~1.0-1.5 Vcm^{-1}.

Diffusing and quenching from a higher temperature would be expected to lead to a greater reduction in responsivity for a given bias and a continuous increase in the maximum bias. Figure 4 compares responsivity as a function of bias for as-grown material and for crystals quenched from 600°C and 700°C. If the mobility is reduced too much by the Cu scattering, however, all the gain in responsivity due to the extended lifetime in the low compensation material will be compensated for by the reduction in mobility.

In order to confirm that the reduction in responsivity is due to the presence of neutral impurity scattering centers and not to defects induced by the quenching, a control sample was quenched from 700°C and evaluated as a detector. The responsivity and maximum bias for this sample were similar to those in the as-grown material.

Conclusions

Cu-diffused ultra-low compensation Ge:Ga detectors can provide higher responsivity than currently available Ge:Ga detectors while maintaining a comparable NEP. By using a high-purity Ge growth facility, which allows for control of electrically active impurities down to $\sim 10^{10} cm^{-3}$, detector material can now be specially designed and modified for optimum detector performance at very low photon backgrounds ($<10^{8}$ photons sec^{-1}).

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References

1. Bratt P R, "Impurity Germanium and Silicon Infrared Detectors", Semiconductors and Semimetals, Willardson R K and Beer A C, eds. (New York: Academic Press) Vol. 12, 39, 1977 and references therein.

2. Hueschen M R, Ph.D. Thesis, U.C. Berkeley, in preparation.

3. Hansen W L and Haller E E, "High-Purity Germanium Crystal Growing", Proc. Materials Research Society 1982 Annual Meeting, Symposium F, Vol. 16, 141-173, Elsevier Science Publishing Co., Inc., New York (1983).

4. Ramdas A K, and Rodriquez S, Reports on Progress in Physics, 44, 1297, (1981).

5. Haller E E, Hueschen M R and Richards P L, J. Appl. Physics 34, 495 (1979).

6. Kitagawa H, Hashimoto K and Yoshida M, J. Journal Appl. Phys. 21, 990 (1982).

7. Haegel N M, Haller E E and Luke P N, Intl. J. Infrared and Millimeter Waves 4, No. 6, 945 (1983).

8. Sclar N, Hoover G J, Milo W C and Pierce R L, "Proc. 1974 IRIS Detector Specialty Group on IR Detectors", p. 247 (1974).

Figure Captions

Figure 1 Responsivity and NEP as a function of bias for as-grown and Cu diffused Ge:Ga with $N_D = 2x10^{10}$ cm^{-3}. T = 3.0 K, F = 20 Hz.

Figure 2 Hall mobility as a function of temperature.

Figure 3 Responsivity and NEP as a function of bias for the Cu-diffused detector and a standard Ge:Ga detector (N_{Ga}=$2x10^{14}$ cm^{-3}, N_D=$1x10^{12}$ cm^{-3}) T = 3.0 K, F = 20 Hz.

Figure 4 Responsivity as a function of bias. T = 3.0 K, F = 20 Hz.

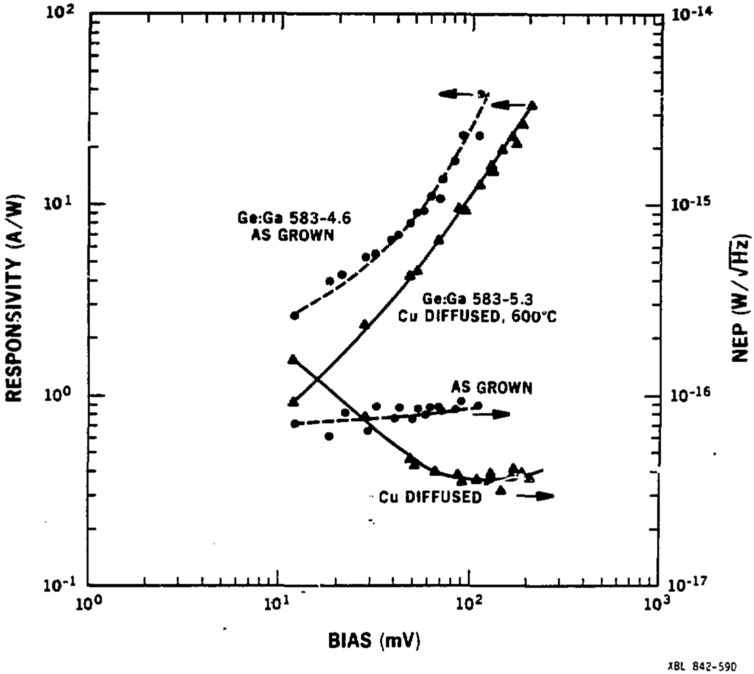
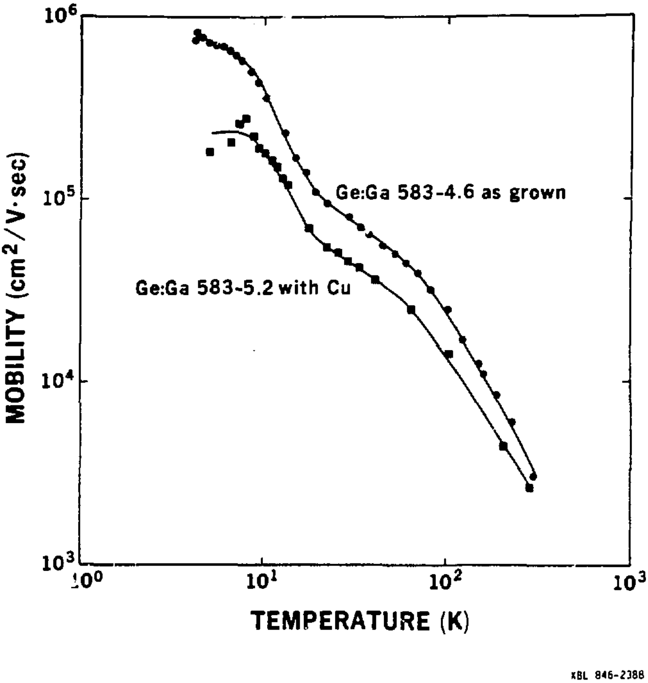
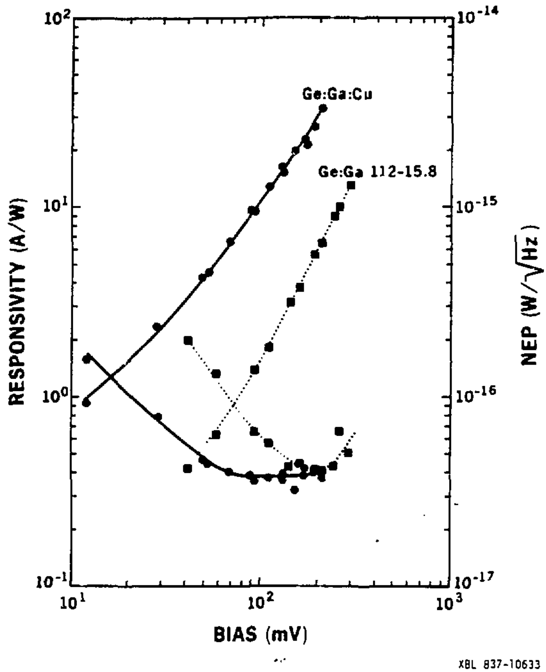

Ge:Ga 583-4.6
AS GROWN
Ge:Ga 583-5.3
Cu DIFFUSED, 600°C
AS GROWN
Cu DIFFUSED
RESPONSIVITY (A/W)
NEP (W/√Hz)
BIAS (mV)
XBL 842-590

Figure 1.



MOBILITY (cm2/V·sec)
10⁶
10⁵
10⁴
10³
Ge:Ga 583-4.6 as grown
Ge:Ga 583-5.2 with Cu
10⁰
10¹
10²
10³
TEMPERATURE (K)
XBL 846-2388

Figure 2.



Ge:Ga:Cu
Ge:Ga 112-15.8
RESPONSIVITY (A/W)
NEP (W/√Hz)
BIAS (mV)
XBL 837-10633

Figure 3.

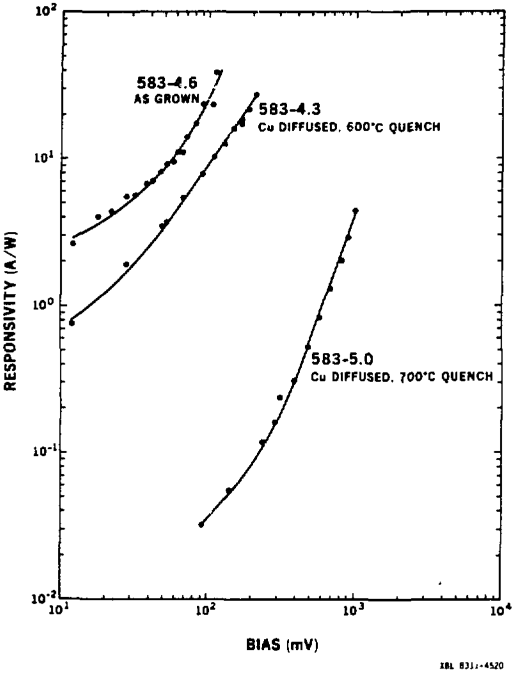

583-4.6
AS GROWN
583-4.3
Cu DIFFUSED, 600°C QUENCH
583-5.0
Cu DIFFUSED, 700°C QUENCH
RESPONSIVITY (A/W)
BIAS (mV)
XBL 8311-4520

Figure 4.