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# The Electronic States of Some Metal Impurities in Germanium

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*Abstract*

Capacitance spectroscopy measurements of the energy levels and majority carrier capture cross sections of deep impurity states associated with S, Zn, Pb and Bi in Ge are presented. Similarities in the electrical properties of these elements with other deep impurities in Ge are discussed.

## Introduction

No general formalism currently exists to predict the physical properties of deep level impurities in semiconductors (Milnes 1973; Grimmeiss 1977). New insights into deep level behaviour are provided by experimental studies, and recent work has indicated that similarities in electrical properties measured for many elements in Si may be due to the existence of families of closely related defects of complicated structure (Lang *et al.* 1980). Initial results in the AAEC laboratories have provided evidence that an analogous situation might exist in germanium (Pearton 1981*a*; 1981*b*). Indeed, the highly pure Ge presently available (with a net electrically active shallow level impurity density of $<5\times10^{13}$ cm$^{-3}$) provides an ideal material for the study of deep level defects. This near perfect lattice, combined with sensitive high-frequency capacitance transient techniques, provides the framework within which a clearer understanding of deep level impurities in semiconductors might be achieved.

In this paper we report the electronic states introduced into Ge by diffusion of S, Zn, Pb or Bi from a surface source, and compare the results obtained with measurements on other impurity centres in Ge. The diffusion of Sn, Si or Ba produced no electrically active states in Ge.

## Experimental Details

The crystals used were pulled from synthetic quartz crucibles in an $H_2$ atmosphere. Hall-effect and capacitance–voltage measurements (1 MHz bridge frequency) at 77 K revealed net shallow level impurity concentrations of $4\times10^{12}$–$6\times10^{13}$ cm$^{-3}$ for the nominally undoped n- and p-type material. Rectangular prism shaped samples (area $\approx0{\cdot}5$ cm$^2$ and thickness $\approx0{\cdot}4$ cm) were cut from the crystals, mechanically polished, and chemically etched to a specular finish in a 4 : 1 mixture of $HNO_3$ : HF. Thin films of S, Zn, Pb or Bi (4 nines purity) or Si or Sn (5 nines purity) were evaporated onto one face from an ohmically heated Mo filament, while Ba was evaporated from a source of the hydroxide. A capping layer of amorphous Ge was then evaporated onto this face for S, Zn, Pb, Bi or Ba diffusions to reduce mass transport during the heating cycle. All other faces were coated in GaIn eutectic alloy, which acts as a gettering agent for unwanted impurities, such as copper.

Diffusions were performed separately on an r.f. induction heated graphite block inside a quartz tube. Heat treatments at 650–700°C for 6–8 hr under flowing $N_2$ gas were used for all the elements. Extensive use was made of control samples, either with or without the capping layer of amorphous Ge. After diffusion and cleaning, contacts were formed to the samples as follows: n-type samples were given Li diffused ohmic contacts (300°C for 10 min) with evaporated Pd Schottky front contacts, whilst the p-type samples were given evaporated In front contacts with evaporated Pd ohmic rear contacts. The use of n- and p-type material enabled both electron and hole traps associated with the metal diffusions to be identified.

The deep level transient spectroscopy (DLTS) technique (Lang 1974) was used to measure the electronic states associated with the impurity metal centres. DLTS scans were performed over the temperature range 15–200 K using a system based on a 1 MHz capacitance bridge and electronic correlator (Miller *et al.* 1975). The energy levels of the impurity states were obtained from Arrhenius plots with the usual $2kT$ correction, where $T$ is the average temperature of the data collection (Miller *et al.* 1977). Capture cross sections and concentrations were directly measured from the dependence of correlator output signal on bias pulse width and amplitude respectively. Concentrations of the observed centres were in the range $7\times10^{10}$–$5\times10^{12}$ cm$^{-3}$. Copper concentrations were $<5\times10^{10}$ cm$^{-3}$ for any sample.

**Table 1. Energy levels and capture cross sections for states associated with S, Bi, Zn or Pb in Ge**
The level energies $E_L$ given are relative to the conduction band $E_c$ for donor (D) states ($E_c-E_L$) or to the valence band $E_v$ for acceptor (A) states ($E_v+E_L$). The band gap $E_c-E_v$ is 0·66 eV for Ge. Energies shown in square brackets are levels listed in the summary by Milnes (1973); s.d. = shallow donors. The corresponding capture cross sections $\sigma_C$ for majority carriers are also given

| S in Ge | | Bi in Ge | | Zn in Ge | | Pb in Ge | |
|---|---|---|---|---|---|---|---|
| $E_L$ (eV) | $\sigma_C$ (cm$^2$) | $E_L$ (eV) | $\sigma_C$ (cm$^2$) | $E_L$ (eV) | $\sigma_C$ (cm$^2$) | $E_L$ (eV) | $\sigma_C$ (cm$^2$) |
| [0·18$^D$] | — | [s.d.] | — | 0·30$^D$ | $1\times10^{-14}$ | 0·39$^A$ | $3\times10^{-13}$ |
| 0·21$^D$ | $5\times10^{-16}$ | 0·17$^A$ | $2\times10^{-16}$ | 0·10$^A$ | $1\times10^{-17}$ | 0·21$^A$ | $2\times10^{-16}$ |
| 0·25$^D$ | $1\times10^{-17}$ | 0·07$^A$ | $7\times10^{-19}$ | [0·095$^A$] | — | 0·17$^A$ | $2\times10^{-15}$ |
| | | | | 0·04$^A$ | $2\times10^{-18}$ | | |
| | | | | [0·035$^A$] | — | | |

## Results

Table 1 lists the energy levels and majority carrier capture cross sections measured for the impurity states associated with S, Bi, Zn or Pb in Ge. The energy level measured relative to the appropriate band (conduction band for donor states and valence band for acceptor states) is given first, followed by D (A) for donor (acceptor) state, and finally the capture cross section of the level for majority carriers (electrons for donor states).

Sulfur-related states have previously been studied by Tyler (1959), who measured a donor state at $E_c-0\cdot18$ eV, using Hall-effect measurements. He also obtained evidence for deeper donor states, but did not give their energy levels. We obtained two deep donor levels for S, $E_c-0\cdot21$ and $E_c-0\cdot25$ eV. The DLTS spectrum for an n-type Ge sample diffused with S is shown in Fig. 1*a*. From the median range of the electrically active concentration profile of these levels, we calculate an approximate diffusion coefficient of $(5\pm3)\times10^{-11}$ cm$^2$ s$^{-1}$ at 700°C for S in Ge. The only other published value is $\approx10^{-9}$ at 920°C (Tyler 1959).

Bismuth is a shallow level donor impurity in Ge, as with the other group V elements. In this experiment concentrations of Bi low enough not to change the polarity of the p-type material were used. Two deep Bi-related states were measured, at $E_v+0{\cdot}07$ and $E_v+0{\cdot}17$ eV, present in concentrations of $\approx 7\times 10^{10}$ cm$^{-3}$ after diffusion at 700°C. The DLTS spectrum for a p-type sample diffused with Bi is shown in Fig. 1*b*. Control samples heated in the same fashion did not show these levels, or any of the other levels measured for the elements studied here.

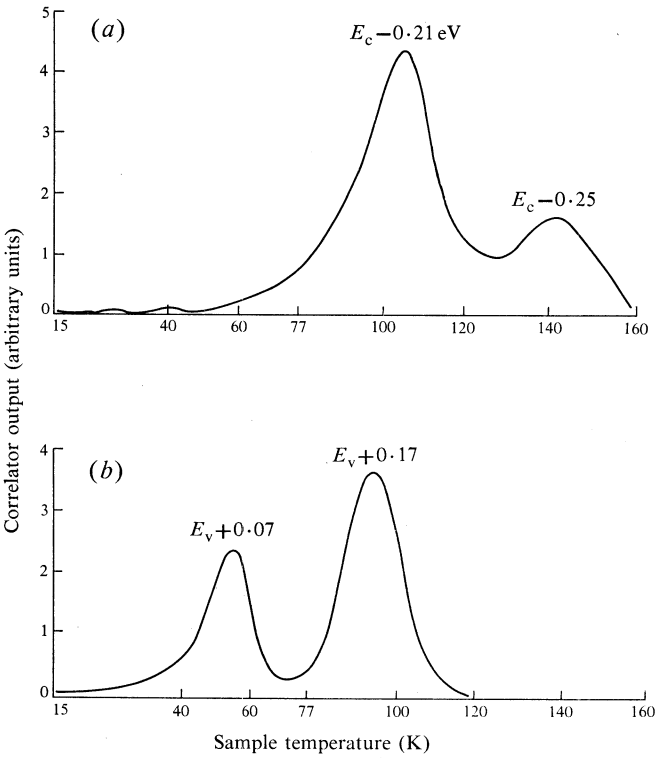


**Fig. 1.** DLTS spectrum for (*a*) an n-type Ge sample diffused with S and (*b*) a p-type Ge sample diffused with a low concentration of Bi. In each case the reverse bias voltage is 5 V and the correlator time constant 10 ms.

We obtained good agreement with previous measurements (Milnes 1973) for two acceptor states associated with Zn in Ge, and also observed a donor state at $E_c-0{\cdot}30$ eV, present at concentrations approximately one-tenth those of the acceptors (Fig. 2). The Arrhenius plots for the defect states measured are displayed in Fig. 3.

As far as the elements in the same column of the Periodic Table as Ge, we measure no electrical activity for Si and Sn, but three acceptor states ($E_v+0{\cdot}17$, $E_v+0{\cdot}21$ and $E_v+0{\cdot}39$ eV) associated with Pb. Also, Pb in Si has been observed to give rise to two deep acceptor levels ($E_v+0{\cdot}37$ and $E_c-0{\cdot}17$ eV) (Chen and Milnes 1980). The diffusion of Ba produced no electrical activity, in agreement with results suggesting that Group II elements in Ge are electrically inactive at concentrations less than $\approx 10^{17}$ cm$^{-3}$ (Borodovski *et al.* 1977).

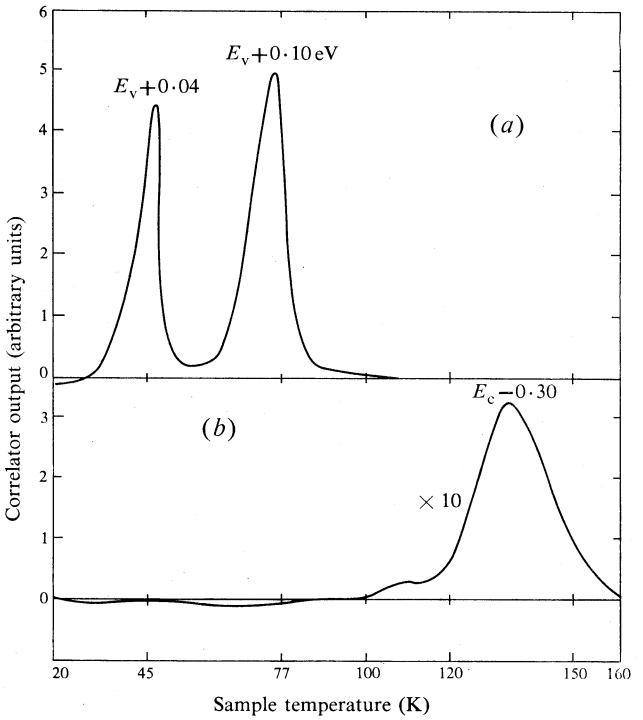


**Fig. 2.** DLTS spectra for (*a*) p-type and (*b*) n-type Ge samples diffused with Zn. The use of both conduction types enables observation of electron and hole traps introduced by the Zn. Here the reverse bias is 2 V and the correlator time constant 10 ms.

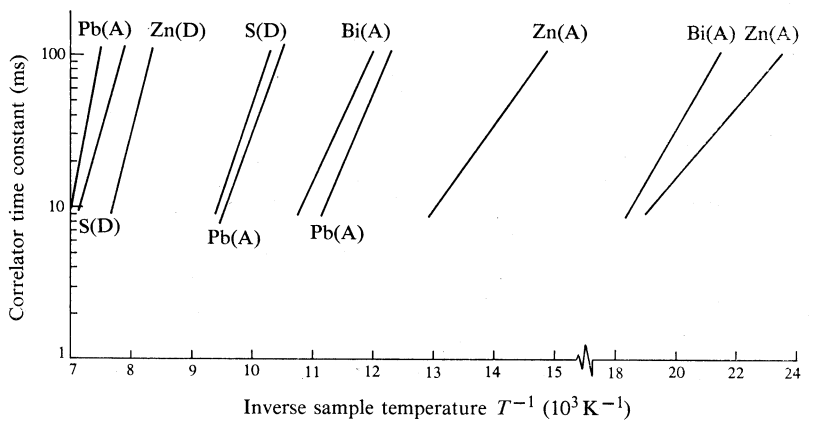


**Fig. 3.** Arrhenius plots for the energy levels associated with the various metal impurities used in this work, where $T$ is the absolute temperature at which the DLTS spectrum occurs for a correlator time constant $t_c$ (inverse of trap emission rate at this temperature). Donor (acceptor) levels are indicated by D (A).

## Discussion

The donor states related to S ($E_c-0{\cdot}21$ and $E_c-0{\cdot}25$ eV) have energies in a similar range to those measured for Au, Pt, Pd, Ni, Tb, Er, Te, Co, Ti, Zr and Fe related donor states in Ge (Pearton 1981*a*; 1981*b*). There appears to be a band of energies from $E_c-0{\cdot}15$ to $E_c-0{\cdot}25$ eV into which many deep metal-related donor states in Ge fall, i.e. at approximately one-third the band gap of the material. The capture cross sections for these states are generally in the range $10^{-16}$–$10^{-18}$ cm$^2$. These facts may be related to the notion that many deep level metal-related centres (at least in Si and Ge) are due to defect complexes of the metal ions with other impurities on lattice defects. This might act to dilute the effect of different metal ions, producing a levelling, or smoothing, of their electrical properties.

Similarly, the deepest acceptor state measured for Bi-related levels ($E_v+0{\cdot}17$ eV) and two of the Pb-related levels ($E_v+0{\cdot}17$ and $E_v+0{\cdot}21$ eV) are similar in energy and capture cross section to acceptor centres related to Te, Cd, Co, Cr, Pd, Tm and Ho (Pearton 1981*a*; 1981*b*). A level at $E_v+0{\cdot}16$ ($\pm 0{\cdot}02$) eV has been previously reported for gamma-irradiated Bi-doped Ge, ascribed to Bi-divacancy complexes (Emtzev *et al.* 1973). It is possible that the large Bi ion forms complexes with vacancies produced during the heat treatment and that these complexes remain stable on cooling. The fact that Pb (which is adjacent to Bi in the Periodic Table, and in the same column as Ge) also displays an acceptor level at $E_v+0{\cdot}17$ eV may be further evidence that many of the energy levels measured are due to impurity–defect associations or possibly lattice strain, rather than specific to the impurity atom.

## Summary

Results showing deep impurity states related to S, Pb, Zn or Bi diffused into Ge are presented. The technique of DLTS measures two donor states for S related centres ($E_c-0{\cdot}21$ and $E_c-0{\cdot}25$ eV), three acceptor states for Pb ($E_v+0{\cdot}17$, $E_v+0{\cdot}21$ and $E_v+0{\cdot}39$ eV), a previously unreported donor state for Zn ($E_c-0{\cdot}30$ eV) and two acceptor states for Bi-related centres ($E_v+0{\cdot}07$ and $E_v+0{\cdot}17$ eV). Some of these impurity states have capture and emission properties similar to deep energy states introduced by many other elements diffused into Ge, strengthening the hypothesis that many metal-related centres in Ge are of complicated structure, rather than simple substitutional or interstitial defects.

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