Neutron transmutation doping of isotopically engineered Ge

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We report a novel approach for obtaining precise control of both p- and n-type dopant concentrations in bulk Ge single crystals. High-purity Ge single crystals of *controlled* $^{74}Ge/^{70}Ge$ isotope composition ratios were grown and subsequently doped by the neutron transmutation doping (NTD) technique. The resulting net-impurity concentrations and the compensation ratios were precisely determined by the thermal neutron fluence and the $[^{74}Ge]/[^{70}Ge]$ ratios of the starting Ge materials, respectively. Application of NTD to seven crystals with $0 \leqslant [^{74}Ge]/[^{70}Ge] \leqslant 4.34$ lead to p-type Ge:Ga,As with compensation ratios in the range 0–0.76. The ability to grow crystals with accurately controlled Ge isotope mixtures allows us to obtain ratios anywhere between 0 and 1 for both p- and n-type doping.

Many semiconductor devices require extremely homogeneous doping and precise control of both majority and minority impurity concentrations (N_{maj} and N_{min}) in order to achieve optimal and consistent performance. Good examples are high voltage, high power Si rectifiers,[1] and Ge cryogenic temperature thermistors.[2] The neutron transmutation doping (NTD) technique has been used for fabricating such devices because it leads to uniform dopant distributions down to the atomic level.[3] NTD Ge thermistors have been widely used as millikelvin range phonon detectors in dark matter searches and neutrino physics,[4] as radiation sensors for astrophysical and radioastronomical observations,[2] and detectors for cosmic ray microwave background measurements.[5] The ability to precisely control both the net-impurity concentration $N_{net}=N_{maj}-N_{min}$ and the compensation ratio $K=N_{min}/N_{maj}$ in bulk Ge is necessary in order to improve the sensitivity of NTD Ge thermistors. (It is important to recognize that controlling N_{net} and K is equivalent to controlling N_{maj} and N_{min}). For example, *hopping conduction*, the temperature-dependent hole conduction mechanism responsible for the signal formation in NTD Ge thermistors, is a strong function of N_{net} and K.[6] We have recently optimized K in NTD Ge thermistors using the method described here, and have achieved an increase in the sensitivity of thermistors working near 300 mK by a factor of 2.6.[7] Some important semiconductor properties that can be studied in samples with well-controlled K are the various ionized impurity scattering mechanisms,[8] and the semiconductor-to-metal (SM) transition.[9] Needless to say, the theories of hopping conduction, ionized impurity scattering, and SM transition have been developed under the assumption that impurities are uniformly, randomly distributed in the semiconductor. The technique described here leads automatically to such semiconductor samples.

Obtaining a crystal with highly uniform majority and minority impurity distributions using one of the conventional bulk doping techniques is impossible. During Czochralski growth, for example, one cannot maintain a fixed concentration ratio of two or more impurities along the growth axes because of their different distribution coefficients. In addition nonuniform concentration fluctuations (called impurity striations) are caused by natural and forced convection of the melt during growth. Since crystal growth from the melt is a high temperature process during which impurities remain mobile for prolonged time, it is possible that two types of impurities with opposite charges attract each other causing further microscopic inhomogeneities.

NTD is the most suitable technique for obtaining uniform dopant distributions in bulk semiconductors. NTD is a low temperature process in which impurities do not become very mobile even during the thermal annealing of the unavoidable fast neutron damage. Any N_{net} can be obtained by adjusting the thermal neutron fluence (i.e., the integrated neutron flux). However, one cannot independently choose K with NTD due to the fixed isotope abundance in naturally occurring semiconductors. For example, NTD of naturally occurring Ge always leads to p-type crystals (Ga acceptors with As and Se compensating donors) with $K=0.32$–0.4.[3,10] The variation in K depends highly on the velocity spectrum of the neutrons from the nuclear reactor. K can be varied systematically if the isotopic composition of the crystal can be controlled. In the past two groups have grown As-doped Ge crystals (n- type) using the Czochralski method and have counterdoped them with Ga acceptors by NTD.[11,12] Both groups were able to produce n-type Ge samples with K between ~ 0 and 0.96. However, the homogeneity of their n-type dopant distribution was questionable since n-type impurity was introduced during melt crystal growth.

In this letter, we will describe the successful control of N_{net} and K by applying the NTD technique to the crystals

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TABLE I. Isotopic composition of ^{70}Ge and ^{74}Ge bars (units: at. %).

Isotopes	^{70}Ge	^{72}Ge	^{73}Ge	^{74}Ge	^{76}Ge
Normal Ge	21.2	27.7	7.7	35.9	7.4
^{70}Ge bar	96.3	3.7			
^{74}Ge bar	0.5	0.07	2.2	96.8	0.33

grown from deliberately chosen mixtures of ^{70}Ge and ^{74}Ge isotopes. ^{70}Ge and ^{74}Ge isotopes were chosen because they transmute into shallow acceptors and donors through NTD, respectively, due to the $^{70}\mathrm{Ge}+n\rightarrow{}^{71}\mathrm{Ge}\rightarrow{}^{71}\mathrm{Ga}$ electron capture and $^{74}\mathrm{Ge}+n\rightarrow{}^{75}\mathrm{Ge}\rightarrow{}^{75}\mathrm{As}$ β decay reactions. Our method leads to majority and minority dopant distributions of extreme uniformity because of the completely random distribution of ^{70}Ge and ^{74}Ge isotopes in our starting crystals. We have recently reported the fabrication of NTD ^{70}Ge:Ga and NTD ^{74}Ge:As samples with $K<0.01$.[13] The present work describes the production of p-type Ge samples of various compensation ratios as a natural extension of our previous work. N-type samples of K between 0 and 1 can be produced simply by increasing the concentration of ^{74}Ge accordingly.

The experimental procedure is as follows. Crystals consisting of controlled mixtures of ^{70}Ge and ^{74}Ge were grown from pieces cut from zone refined isotopically enriched ^{70}Ge and ^{74}Ge bars of isotopic compositions given in Table I. Our typical crystal size is $\sim$ 4 cm in length, 6 mm in diameter, resulting in 4 g of weight. A detailed description of our crystal growth method has been reported in Ref. 14. The mass ratio of the ^{70}Ge and ^{74}Ge starting charges determines the $[^{74}\mathrm{Ge}]/[^{70}\mathrm{Ge}]$ ratio in our crystal

$$\frac{[^{74}\mathrm{Ge}]}{[^{70}\mathrm{Ge}]}=\frac{5.13\,\mathrm{g/cm^3}\times(\text{mass of the }{}^{74}\text{Ge piece})\times 96.3\%}{5.43\,\mathrm{g/cm^3}\times(\text{mass of the }{}^{70}\text{Ge piece})\times 96.8\%}. \quad (1)$$

Volume densities of 5.13 and 5.43 g/cm^3 for our ^{70}Ge and ^{74}Ge bars, respectively, are used in accordance with the composition shown in Table I. We also assume that the number of Ge atoms per unit volume is the same for ^{70}Ge and ^{74}Ge, because the measured isotope shift of Ge lattice constant is negligibly small.[15] Prior to the growth, ^{70}Ge and ^{74}Ge pieces were melted together in a rf heated ultrapure graphite boat, in order to assure complete mixing of the different isotopes. After growing seven Ge crystals with different $[^{74}\mathrm{Ge}]/[^{70}\mathrm{Ge}]$ ratios, a 1-mm-thick wafer was cut from each crystal (samples A–G in Table II), and its isotopic composition was measured by secondary ion mass spectroscopy (SIMS). Uniform isotope distribution through the crystals was confirmed by comparing the isotopic composition at both ends of several crystals. All wafers were then thermal neutron irradiated for exactly the same duration, 4 h, at the University of Missouri Research Reactor. The thermal neutron flux at the irradiation position was 6.43×10^{12} cm^{-2} s^{-1}. The irradiated wafers were annealed for 10 s at 650 °C in a N_2 atmosphere to eliminate electrically active radiation defects formed by unavoidable fast neutrons. Our recent deep level transient spectroscopy study has confirmed that the post-annealed samples contain less than a total of 3×10^{12} cm^{-3} deep majority and minority carrier traps. After seven half-lives of the ^{71}Ge to ^{71}Ga decay reaction, the temperature dependence of the free hole concentration was measured by Hall effect in order to determine the Ga and As concentrations in each sample.

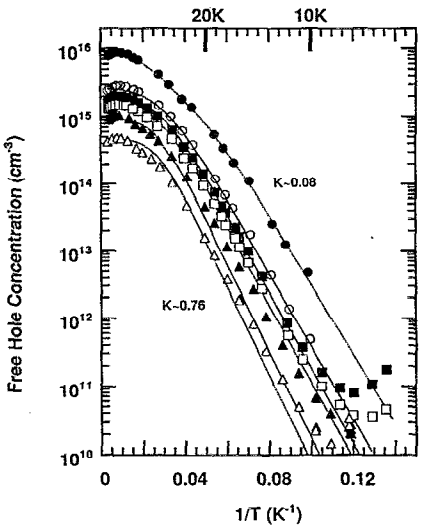

FIG. 1. Temperature dependence of the free hole concentration in samples B (●), C (○), D (■), E (□), F (▲), and G (△). Solid curves are fits obtained from Eq. (3).

Table II shows the isotopic composition measurement results obtained by SIMS. The $[^{74}\mathrm{Ge}]/[^{70}\mathrm{Ge}]$ ratios in the range from 0 to 4.34 agree well with the values we estimated with Eq. (1). We can predict the concentration N_x (cm^{-3}) of Ga and As for a given thermal neutron fluence n (cm^{-2}) for each sample by inserting the measured isotopic composition values into the following expression:

TABLE II. Summary of SIMS composition measurement and predicted and measured impurity concentrations after 4 h neutron irradiation.

	Isotope composition measured by SIMS (unit in at. %)						Predicted concentrations after NTD based on SIMS results (unit in $\times10^{15}$ cm^{-3})				Fitted concentrations after NTD (unit in $\times10^{15}$ cm^{-3})			
Sample	^{70}Ge	^{72}Ge	^{73}Ge	^{74}Ge	^{76}Ge	$[^{74}\mathrm{Ge}]/[^{70}\mathrm{Ge}]$	[Ga]	[As]	[Ga]−[As]	K	[Ga]	[As]	[Ga]−[As]	K
A	96.3	3.7				0	17.0		17.0	~0	17.0	0.2	16.8	0.012
B	65.8	2.6	0.7	30.7	0.2	0.47	7.30	0.60	6.70	0.082	10	3.3	6.7	0.082
C	32.9	1.5	1.4	64.0	0.2	1.94	3.65	1.25	2.40	0.34	3.95	1.35	2.6	0.34
D	29.5	1.2	1.5	67.6	0.2	2.29	3.27	1.32	1.95	0.40	3.27	1.32	1.95	0.40
E	25.5	1.1	1.8	71.3	0.3	2.80	2.83	1.39	1.49	0.49	2.83	1.39	1.49	0.49
F	21.8	0.9	1.7	75.4	0.2	3.46	2.42	1.47	0.95	0.61	2.42	1.47	0.95	0.61
G	18.2	0.8	1.7	79.0	0.3	4.34	2.02	1.54	0.48	0.76	2.02	1.54	0.48	0.76

$$N_x = N_{iso}\sigma_c n, \tag{2}$$

where N_{iso} is the concentration of particular isotopes (cm^{-3}) and σ_c is the thermal neutron capture cross-section of each nucleus (cm^2). The thermal capture cross-section values used in this work are 2.74×10^{-24} and 4.82×10^{-25} cm^2 for the ^{70}Ge and ^{74}Ge isotopes, respectively. The predicted concentrations, shown in Table II, are to be compared with the [Ga] and [As] measured by the Hall effect. Figure 1 shows the temperature dependence of the free hole concentration in samples A–G. A magnetic induction of 3000 G was used for all measurements and a Hall factor of unity (high magnetic field limit) is assumed for $T<100$ K. The standard free carrier statistics equation for semiconductors[16] doped by shallow acceptors and compensated by donors is used to fit each curve

$$p = \frac{[2(N_A - N_D)]}{\{[1+(N_D/gN_V)\exp(E_A/k_BT)] + \sqrt{[1+(N_D/gN_V)\exp(E_A/k_BT)]^2 + (4/gN_V)(N_A-N_D)\exp(E_A/k_BT)}\}}, \tag{3}$$

where p is the free hole concentration, N_A and N_D are the acceptor and donor concentration, respectively, N_V is the effective valance band density of states, $g=4$ is the spin degeneracy for an acceptor, and E_A is the acceptor ionization energy. E_A of Ga in Ge is 11.07 meV[17] for [Ga]$<10^{15}$ cm^{-3} samples, but it decreases when [Ga]$>10^{15}$ cm^{-3}. Therefore, in the first step of our fitting procedure, we set N_A and N_D equal to the [Ga] and [As], respectively, as given by our SIMS results. E_A is used as a fitting parameter in Eq. (3). By this method, excellent fits are obtained for samples A, D, and E with $E_A=9$, 9.7, and 9.8 meV, respectively, as shown in Fig. 1. Deviations of the experimental results for $T>100$ K and for the very low temperature region are due to deviations of the Hall factor from 1 and the onset of hopping conduction, respectively. The predicted net-acceptor values [Ga]–[As] also agree very well with the Hall measurements in samples F and G. However, in the $T<20$ K region the freeze-out curve cannot be fitted, possibly due to hopping conduction or again to the deviation of the Hall factor from 1. In the case of samples B and C, the predicted values of [Ga] and [As] needed to be modified slightly in order to fit the data. After the modification, fits were obtained for samples B and C with E_A of 9 and 9.3 meV, respectively. Because the effect of hopping conduction is very small even at 10 K, the measurement error in N_A and N_D, i.e., [Ga] and [As] obtained by fitting is minimal for samples B and C.

Values of [Ga] and [As] obtained by fitting the Hall results after NTD are listed in Table II. The predicted compensation ratios from the SIMS results agreed perfectly with the measured compensation after NTD for all samples except sample A. There is a large uncertainty in the [As] of sample A obtained from the fit due to the effect of hopping conduction. The values of [Ga] and [As] calculated from Eq. (2) agree very well with the fitted values obtained from Hall measurements. Thus our proposed method, the neutron transmutation doping of isotopically controlled Ge, is proven to be an effective approach of controlling both N_{net} and K in Ge.

In summary, we have shown that the combination of NTD and isotopic control of Ge leads to predictable and highly uniform majority and minority dopant concentrations in Ge. The measured temperature dependence of the free hole concentration curves in all p-type samples agree very well with the theoretical fits, i.e., all samples doped by NTD in this work must have extremely homogeneous majority and minority impurity distributions. This new approach to obtain precise and uniform dopant concentrations is promising for a range of solid state studies (transport, metal-semiconductor transition, etc.) and semiconductor devices.

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