DEVELOPMENT OF BORON AND PHOSPHORUS LIQUID-METAL-ION SOURCES

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Résumé - Des sources d'ions à métal liquide (LMIS) de (B) et (P) ont été développées pour l'implantation sans masque dans le silicium. La source de (B) qui emploie un émetteur de carbone ou de carbure et un alliage à base de Ni-B a une durée de vie de plus de 250 heures. La source de (P) utilisant l'alliage Cu-P permet plus de 20 heures de fonctionnement. Les ions issus de ces sources sont analysés en masse et en énergie. Des effets isotopiques ont été observés pour l'émission ionique de B. Des essais préliminaires d'implantation de B^+ dans Si ont été entrepris en utilisant une colonne ionique avec séparateur de masse.

Abstract - Boron (B) and phosphorus (P) liquid-metal-ion (LMI) sources have been developed for maskless implantation in silicon. The B-LMI source, which employs a carbon or carbide emitter and a Ni-B base alloy as its source material, has a lifetime of more than 250 hours. The P-LMI source utilizing a Cu-P alloy achieves a lifetime of more than 20 hours. The ions emitted from these sources are investigated by mass and energy analyses. Isotope effect has been observed for B ion emission with a B-LMI source. Focused B^+ implantation in Si was preliminarily carried out using a mass-separated microbeam column.

1. Introduction

LMI sources are now being actively investigated due to the potentially enormorus advantages they offer in focused-ion-beam (FIB) technology, such as maskless implantation, microfabrication, and submicron analysis /1-4/. Considerable interest has also been shown in the diversity of ion species LMI sources provide. For ion implantation into Si semiconductors, B, As, and P are the most important dopants. However, it is difficult to construct LMI sources from these materials due to their high melting point (for B), high vapour pressure (for As and P), or strong corrosive effect on most metals (for B). Several LMI sources that use eutectic alloys as the source material have been reported to date /5-7/. For GaAs semiconductors, LMI sources for Be and Si ions have also been developed by employing eutectic alloys /5,8,9/.

Recently, B- and P-LMI sources have been developed by the authors /10,11/. The present paper briefly describes these sources with new additional data on ion emission characteristics. Evidence of isotope effect in the B-LMI source is also presented. Further, preliminary experiments on B^+-FIB implantation into Si using a mass-separated microbeam column /12/ with maximum beam energy of 20 keV are described. Finally, the high dose-rate effect in FIB implantation /13/ is discussed.

2. B- and P-LMI sources

The LMI source for B and P ions consists of a needle emitter, heater and extractor. Molten source-material mounted on the heater covers the emitter and stably flows to the emitter tip during ion emission. For the B-LMI source /10/, a combination of carbon or carbide needles and Ni-B base alloys as the source material was used. Little reaction is produced between these materials, so they provide a source lifetime of more than 250 hours. For the P-LMI source /11/, a combination of metal needle and Cu-P alloy was employed. A source lifetime of more than 20 hours was achieved, which was mainly restricted by selective evaporation of the P element due to its high vapor pressure. Thus, there is much room for improvement of the P source lifetime.

Ions emitted from the source were investigated by mass and energy analyses using a double-focusing mass spectrometer with an energy resolution of $\Delta E = 1.1$ eV at $E = 3.2$ keV. This resolution was calibrated using surface-ionized Na^+ beams.

Typical mass spectra for ions emitted from the liquid $Ni_{45}B_{45}Si_{10}$ alloy at $I_t = 25$ µA and Cu_3P alloy at $I_t = 80$ µA are shown in Figs. 1 (a) and (b), respectively. Here, I_t is total emission current. Operating temperature for these sources was 900 - 950 °C for the B source and 750 - 800 °C for the P source. The B^+ and P^+ ion intensities were 25 - 35 % and about 10 % of total ion intensity, respectively, depending on operating conditions.

Typical energy distributions for $^{11}B^+$, $^{58}Ni^+$, and $^{28}Si^+$ ions from the Ni-B-Si alloy are shown in Fig.2 for $I_t = 40$ µA. The origin of the energy axis is estimated, rather than calibrated. Similar experiments for the Cu-P alloy were carried out. Typical results of full-width-at-half-maximum (FWHM) value, ΔE, for various ions are given in Table 1. It was found that ΔE values for doubly-charged ions are, in general, have a narrower range than those for singly-charged ions, as pointed out in a previous paper /14/.

The ΔE vs. I_t results for various ions, i.e. B^+ for Ni-B-Si alloy, P^+ and Cu^+ for Cu-P alloy, and Ga^+ for pure Ga, are summarized in Fig. 3. As shown, there is a strong mass-dependence, with lighter ions having a narrower ΔE.

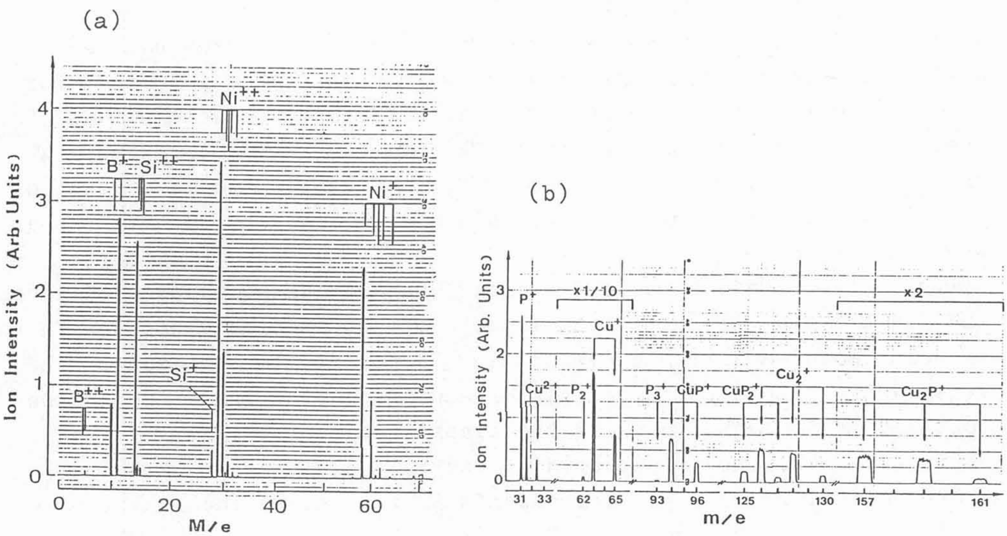

Fig.1 Typical mass spectra from LMI sources; (a) Ni-B-Si and (b) Cu-P alloys.

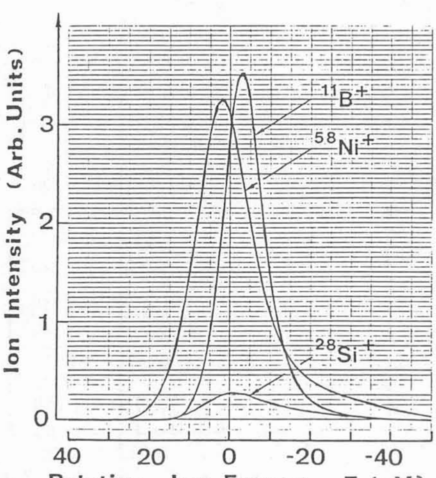

Fig.2 Typical energy distributions of B, Ni, and Si ions.

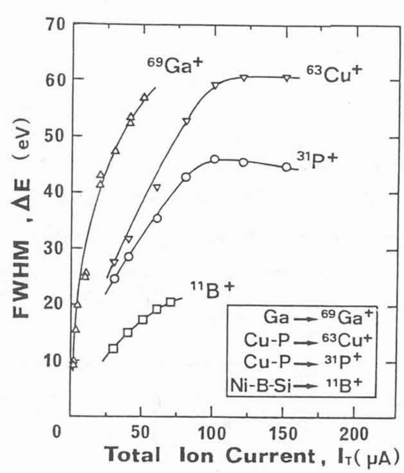

Fig.3 ΔE vs. I_t for various LMI sources.

3. Isotope effect on B ion emission

Isotope effect on B ions emitted from the B-LMI source has been observed. The B^{++} ion intensity is as weak as 1/30 - 1/50 that for B^+ at I_t=15-100μA, but there is a certain difference between P_{10} and P_{11}, where P_m is the intensity ratio of $^mB^{++}$ to ($^mB^+$ + $^mB^{++}$). Figure 4 shows the experimental ΔP values (= P_{11} - P_{10}) plotted as a function of P (= P_{11}). As shown, the P_{11} values are larger by 13 - 17 % than the P_{10} values.

The post-ionisation model for field evaporation proposed by Haydock and Kingham /15/ predicts such isotope effect when an element with two or more isotopes is field evaporated. According to that model, the less-massive isotopes travel faster and thus spend less time in the post-ionisation zone in which the transition from the singly- to doubly-charged ions is expected to occur.

The solid line in Fig.4 corresponds to the theoretical curve based on this model, expressed as $\Delta P = (1/2)(\Delta M/M_b)P_b$ for $\Delta M \ll M_b$ and $P_b \ll 1$. Here, $\Delta M = M_b - M_a$ and M_m represents the mass of isotope m. The post-ionisation model explains the present isotope effect fairly well, although there are some discrepancies between experiment and theory. A similar isotope effect has been observed for field evaporation of FeB and CoB metallic glasses by Menand and Kingham /16/. A more detailed discussion will be presented elsewhere.

Table 1 ΔE values for various ions emitted from Ni-B-Si and Cu-P LMI-sources at I_t = 30 μA.

		ΔE (eV)	
		+	++
Ni-B-Si	^{11}B	12	-
	^{28}Si	19	12
	^{58}Ni	17	17
Cu-P	^{31}P	25	-
	^{63}Cu	28	22

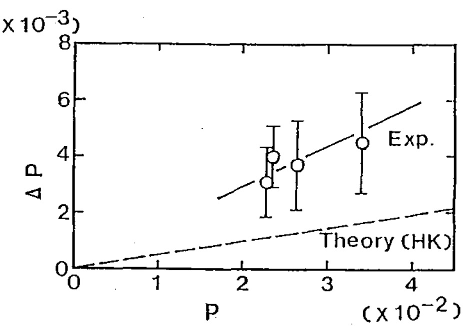

Fig.4 Difference in post-ionisation probabilities of $^{10}B^+$ and $^{11}B^+$, ΔP, as a function of post-ionisation probability of $^{11}B^+$, P. (Broken line corresponds to the theoretical curve.)

4. FIB implantation

Preliminary experiments on FIB implantation have been carring out using a mass-separated microbeam column, the details of which have been described elsewhere /12/. This column has the ability to produce sub-μm beams with energies of upto 20 keV and high current densities, J, e.g. several tens of mA/cm^2 for B^+ beam. These J values are about three orders higher in magnitude than those for a conventional implanter using an unfocused beam.

Figure 5 shows the calculated maximum temperature at the center of a steady-state unscanned FIB for Si and GaAs targets based on the analytical form of Nissim et al /17/. In the calculation, a target back-surface temperature of 25 °C and temperature-dependent thermal conductivity expressed by $K(T) = A/(T - B)$ are assumed. Here, A = 299 W/cm and B = -174 °C for Si, and A = 91 W/cm and B = -182 °C for GaAs. It should be noted that even a 100 keV unscanned beam of 1 μm in diameter with $J = 10\ A/cm^2$ is expected to increase a Si target temperature from 25 °C to only about 50 °C. No significant FIB-heating has already pointed out in the previous /2/.

Recently, a high dose-rate effect has been observed for B^+ FIB implantation into Si, that is, high electrical activation in the annealed implanted-layer has been resulted from enhancement of the amorphous zone /13/. This enhancement is presumably brought about by overlapping of the damage zone surrounding the ion path within some lifetime of its shrinkage, not by FIB heating and self-annealing.

5. Conclusions

B- and P-LMI sources have been developed for maskless implantation into Si semiconductors. The B-LMI source, using a combination of a carbon or carbide emitter and a Ni-B base alloy as its source material, has a lifetime of more than 250 hours and provides a B^+ emission current of 25 - 35 % the total emission current.

Isotope variations in B ion emission have been observed. The proportion of $^{10}B^{++}$ to ($^{10}B^+$ + $^{10}B^{++}$) is 1/30 - 1/50, which is 13 - 17 % smaller than for $^{11}B^{++}$. This isotope effect was predicted by the post-ionisation model for field evaporation proposed by Haydock and Kingham/15/, although there are certain discrepancies between the experimental results and theory.

A P-LMI source utilizing a Cu-P alloy has also been developed. P^+ ion emission current is about 10 % of total emission current in this source and its lifetime is more than 20 hours.

Emission characteristics for the B- and P-LMI sources have been investigated by mass and energy analyses. Preliminary experiments on FIB implantation were also carried out using a mass-separated microbeam column. In these experiments, high dose-rate effect was observed.

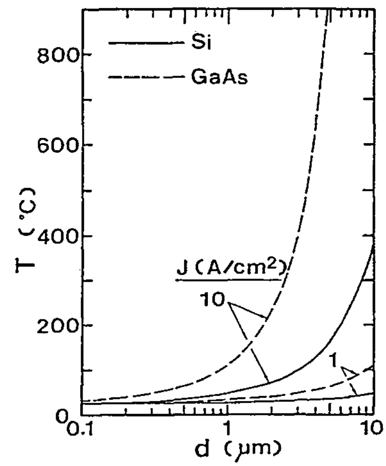

Fig.5 Calculated maximum temperature at the center of a 100 keV steady-state unscanned beam for Si and GaAs targets

References

1 R.L.Kubena, C.L.Anderson, R.L.Seliger, R.A.Jullens, E.H.Stevens, and I.Lagnado: J. Vac. Sci. Technol. 19(1981)916
2 W.L.Brown and A.Wagner: in Proc. of Int. Ion Engineering Congress ISIAT'83 & IPAT'83 (Kyoto, 1983)
3 M.Komuro: Thin Solid Films 92(1982)155
4 Y.Bamba, E.Miyauchi, H.Arimoto, K.Kuramoto, A.Takamori, and H.Hashimoto: Japan. J. Appl. Phys. 22(1983)L650
5 V.Wang, J.W.Ward, and R.L.Seliger: J. Vac. Sci. Technol. 19(1981) 1158
6 K.Gamo, T.Ukegawa, Y.Inomoto, K.K.Ka, and S.Namba: Japan. J. Appl. Phys. 19(1980)L595
7 K.Gamo, T.Ukegawa, Y.Inomoto, Y.Ochiai, and S.Namba: J. Vac. Sci. Technol. 19(1981)1182
8 E.Miyauchi, H.Hashimoto, and T.Utsumi: Japan. J. Appl. Phys. 22 (1983)L225
9 K.Gamo, T.Matsui, and S.Namba: Japan. J. Appl. Phys. 22(1983)L692
10 T.Ishitani, K.Umemura, S.Hosoki, S.Takayama, and H.Tamura: J. Vac. Sci. Technol. (in press)
11 T.Ishitani, K.Umemura, and H.Tamura: Japan. J. Appl. Phys. 23 (1984)L330
12 T.Ishitani, K.Umemura, and H.Tamura: Nucl. Instrum. Methods 218 (1983)363
13 M.Tamura, S.Shukuri, S.Tachi, T.Ishitani, and H.Tamura: Japan. J. Appl. Phys. 22(1983)L698
14 L.W.Swanson: in Proc. of Int. Ion Engineering Congress ISIAT'83 & IPAT'83 (Kyoto, 1983)p.325
15 R.Haydock and D.R.Kingham: Phys. Rev. Lett. 44(1980)1520
16 A.Menand and D.R.Kingham: J. Phys. D: Appl. Phys. 17(1984)203
17 Y.I.Nissim, A.Lietoila, R.B.Gold, J.F.Gibbons: J. Appl. Phys. 51 (1980)274