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Percolation network of PdGe phase formed on Ge surface by high-current Pd-ion implantation

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Abstract. High-current Pd-ion implantation technique was employed to synthesize Pd germanide on Ge wafers, using a metal vapour vacuum arc (MEVVA) ion source. The implantation was conducted with an extracted voltage of 34 kV, beam current densities of 17.7 and 53 μA cm^{-2} and at a fixed dose of 2×10^{17} ions cm^{-2}. It was found that implantation with a current density of 17.7 μA cm^{-2} could directly synthesize the equilibrium PdGe phase on the Ge surface and that the formed germanide loosely dispersed on the surface. Interesting, in the case of implantation with the current density of 53 μA cm^{-2}, the formed PdGe grains organized themselves in a fractal pattern with a dimension close to the percolation threshold of 1.90, and the sheet resistivity was therefore significantly reduced down to 59 $\Omega\ \square^{-1}$. The formation of the PdGe phase as well as the percolation network under MEVVA implantation is also discussed.

1. Introduction

Recently, interest in field effect transistors built on semiconductors other than silicon comes from a growing need for high-speed, low-power digital and analogue circuits. Germanium, silicon and GaAs are nowadays the three most important semiconductor materials. For device applications, germanium is important due to its high electron and hole mobilities, making a high-speed complementary field effect transistor possible [1].

Compared with the extensive studies of metal silicide, formation of metal germanide has so far received less attention [2–7]. Consequently, to gain a better understanding of metal germanide formation is very important not only for developing germanium-based detector and integrated circuits but also for novel applications in various fields. For example, metal contacts for strained (Ge, Si)/Si heterostructures are very promising to be applied in optical communications, integrated optics on silicon etc. While preparing metallic contacts on GaAs, metal germanides are also thought of as particularly interesting candidates [8–10].

In 1985, a metal vapour vacuum arc (MEVVA) ion source was invented [11], which is capable of providing almost all the metal-ion species with a high current density. Generally, an implanter with a MEVVA ion source provides metal ions with multiple charges, as such an implanter is not equipped with a mass analysis magnet. The purity of the ions therefore depends on the purity of the metal of which the cathode is made. The MEVVA ion source is currently also available in the People's Republic of China. For instance, a MEVVA ion source established in the early 1990s can provide a current density up to 150 μA cm^{-2} on a 10 cm diameter target at an extracted voltage of 50 kV [12]. Using the MEVVA ion source, it is feasible to conduct metal-ion implantation up to a dose of 10^{18} ions cm^{-2}, corresponding to a doping content of several tens of at.%, within an hour.

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The idea of directly synthesizing metal silicide on Si by metal vapour vacuum arc (MEVVA) ion implantation was initiated by the authors' group in the early 1990s. It is thought that the high-current metal ions can not only provide the metal species to fulfill the chemical stoichiometry requirement, but also induce a simultaneous beam heating necessary for forming the respective metal silicide on silicon. It follows that neither *in situ* heating during implantation nor post-annealing was needed in ion beam synthesis using MEVVA implantation. In other words, a single-step implantation technique for metallization is possible and has been employed to successfully obtain equilibrium C54–$TiSi_2$ [5], $FeSi_2$ [6] and $CoSi_2$ [7] layers of fine quality. The main idea of this study is to apply MEVVA implantation to investigate the possibility of directly synthesizing the Pd germanide. According to the published literature, in the Pd–Ge system, the first growing phase upon solid-state reaction at 100–200 °C was found to be Pd_2Ge and the PdGe would be the dominating phase only after annealing at a temperature exceeding 200–250 °C for long time; the formation of Pd_2Ge and PdGe was diffusion controlled with somehow a similar activation energy of about 1.5 eV [13–15]. It is noted that these two phases are both Pd rich up to 50 and 66 at.%, implying that an exact stoichiometry of these phases is not easy to fulfill by ion implantation. The objective of this study is to synthesize the Pd germanide by high-current Pd-ion implantation into Ge with a deposited Pd overlayer.

2. Experimental procedure

The germanium wafers used in this study were Ge(111) with 10 mm diameter and resistivity of 5–10 Ω cm. The samples were cleaned by a standard chemical procedure and then were deposited with a 10 nm Pd overlayer by electron evaporation at a vacuum level of the order of 10^{-4} Pa. The thickness of the Pd overlayers was chosen so that the damage peak caused by implantation would be located near the Pd–Ge interface. The wafers were directly adhered on a steel-made sample holder in the target chamber of the MEVVA implanter with a vacuum level of 3×10^{-3} Pa. No special cooling was provided for the sample holder during implantation. As the MEVVA implanter has no analysing magnet, the extracted Pd ions were analysed to consist of 23% Pd^+, 67% Pd^{2+}, 9% Pd^{3+} and 1% Pd^{4+}, respectively. As an extracted voltage of 34 kV was applied in this study, the corresponding energies of the implanting Pd ions were then 34 keV, 68 keV, 102 keV and 136 keV, respectively. The samples were implanted with two current densities of 17.7 and 53 μA cm^{-2} at a nominal dose of 2×10^{17} ions cm^{-2}. An NiAl–NiCr thermocouple was attached to the un-implanted area of the Ge wafer to measure the temperature rise during implantation.

After implantation, x-ray diffraction (XRD) was performed to identify the MEVVA-synthesized Pd germanide by a D/max-RB diffractometer operated with a Cu radiation of 1.541 78 Å at 40 kV and 100 mA. Rutherford backscattering spectrometry (RBS) was employed with 2.023 MeV He ions to measure the depth profiles of the implanted Pd atoms. The sheet resistances of the Ge wafers before and after implantation were measured by a D41-3 type four-point-probe instrument. Scanning electron microscopy (SEM) was employed to examine the morphology of the samples.

3. Results and discussion

3.1. Formation of PdGe

In the Ge samples with a 10 nm Pd overlayer implanted by Pd ions with current densities of 17.7 and 53 μA cm^{-2}, Pd germanide was detected by x-ray diffraction analysis and figure 1(a) and (b) displays the XRD spectra of the samples implanted at a fixed dose of 2×10^{17} cm^{-2}

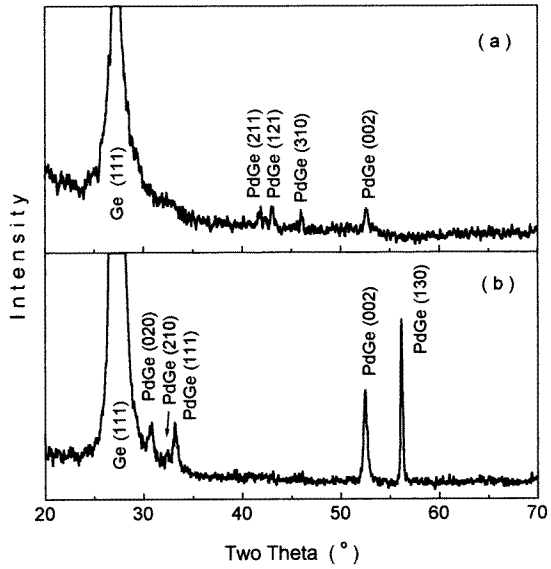

Figure 1. XRD pattern of Ge wafer implanted by Pd ions with current densities of (a) 17.7 μA cm^{-2} and (b) 53 μA cm^{-2} at a fixed ion dose of 2×10^{17} ions cm^{-2}.

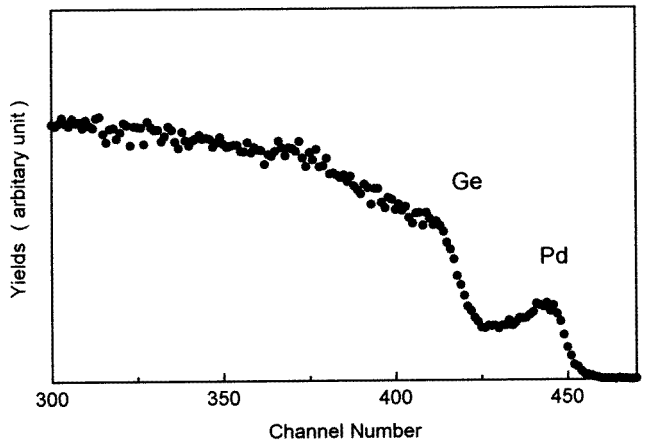

Figure 2. RBS spectrum of the sample implanted with a current density of 53 μA cm^{-2} to an ion dose of 2×10^{17} ions cm^{-2}.

with respective current densities. As shown in figure 1(a), the PdGe phase was detected in the sample implanted by Pd ions with a current density of 17.7 μA cm^{-2}, yet the crystallinity of the formed germanide is not so good, as four diffraction lines seen in the spectrum are quite weak. By implanting Pd ions with an increased current density of 53 μA cm^{-2}, the PdGe was also formed and featured an improved crystallinity, as evidenced by more and stronger diffraction lines shown in figure 1(b).

Figure 2 illustrates an RBS spectrum for the sample implanted with a current density of 53 μA cm^{-2} to a dose of 2×10^{17} cm^{-2}. From figure 2, the maximum Pd concentration was deduced to be 20 at.%, which is far below the exact stoichiometry of PdGe, which can probably

Table 1. The characterization results of Pd-ion implantation into Ge(111) wafers at an extracted voltage of 34 kV with varying current density and a fixed nominal dose of 2×10^{17} ions cm^{-2}; w, m and s stand for weak, medium and strong, respectively, and v means very.

Current density (μA cm^{-2})	Implanting time (min)	Temperature rise (°C)	Interplanar spacing d (Å) and diffraction lines from PdGe	Stoichometry Pd:Ge (by RBS)	Sheet resistance ($\Omega\,\square^{-1}$)
17.7	60	RT-160	2.1543 (211)w 2.1017 (121)w 1.9714 (310)vw 1.7373 (002)w	1:9	135
53	29	RT-300	2.8988 (020)m 2.7560 (210)w 2.7010 (111)m 1.7410 (002)s 1.6359 (130)s	1:4	59

be attributed to the sputtering effect and radiation enhanced diffusion upon high current ion implantation.

According to an estimation by the method suggested by Zhu and Liu [16], as the thermal conducting condition in this study was similar to that of Zhu and Liu, the temperature rise of the Ge wafers implanted with a current density of 17.7 μA cm^{-2} was about 160 °C, which was confirmed by the thermocouple measurement. In other words, MEVVA implantation can synthesize the PdGe phase on Ge at a temperature lower than 200 °C within an hour, while in the solid-state reaction the reaction must be beyond 200 °C and requires a very long time. When implanting with a current density of 53 μA cm^{-2}, the temperature rise was about 300 °C, which as mentioned above improved the cystallinity of the formed PdGe.

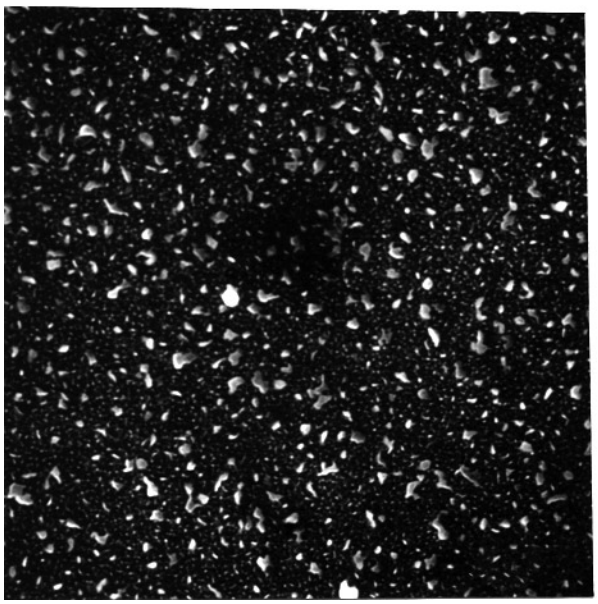

Figure 3. SEM photo of the samples implanted with a current density of 17.7 μA cm^{-2} at an ion dose of 2×10^{17} ions cm^{-2}.

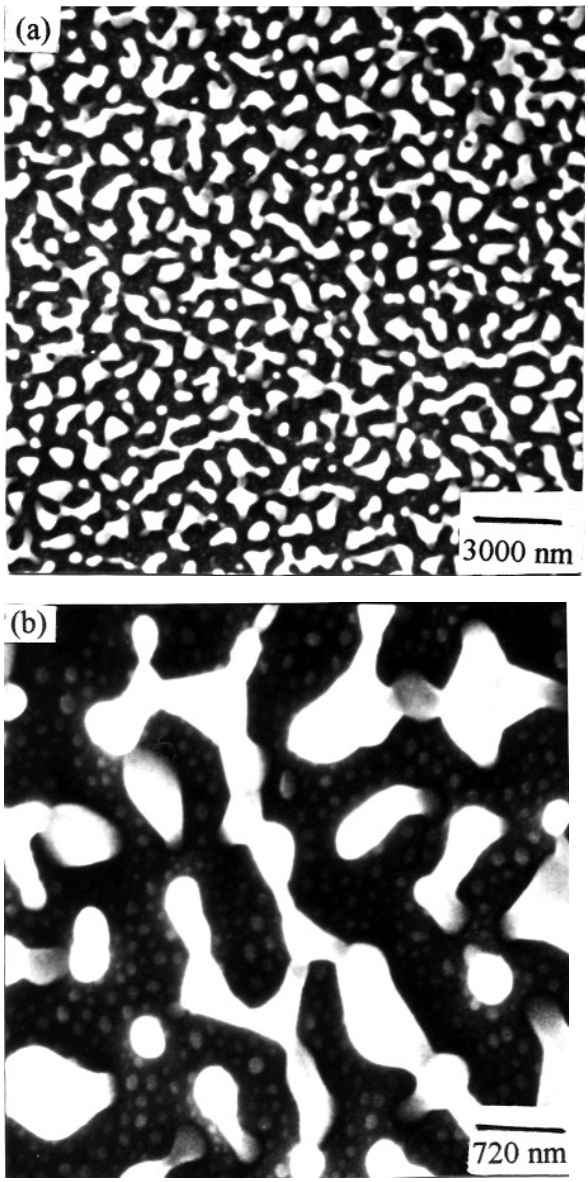

Figure 4. SEM photos of the samples implanted with a current density of 53 μA cm^{-2} at an ion dose of 2×10^{17} ions cm^{-2} with different magnifications.

3.2. Morphology of the formed PdGe

Table 1 lists the characterization results of the Pd-ion implanted Ge at a fixed dose of 2×10^{17} ions cm^{-2} with current densities of 17.7 and 53 μA cm^{-2}. As listed in table 1, the sheet resistivity of the samples implanted by 17.7 μA cm^{-2} was 135 $\Omega\,\square^{-1}$, and that of the sample implanted by 53 μA cm^{-2} was 59 $\Omega\,\square^{-1}$. As a reference, the resistivity of the Ge wafers was measured to be 450–550 $\Omega\,\square^{-1}$.

SEM examination revealed some interesting morphology of the formed PdGe in the implanted samples and two typical SEM photos are shown in figure 3 and figure 4. The

magnification of the SEM photos in figures 3 and 4(a) was 1:5000, and that in figure 4(b) was 1:20 000. From figures 3 and 4, one can see that in the low-current implantation case the formed PdGe phase was rippled and loosely dispersed on the Ge surface, and that in the high-current density case PdGe phases grew considerably and some of them became inter-connected which can be clearly observed in figure 4(b). The loose pattern consisting of PdGe phase shown in figure 3 is attributed to a low forming temperature induced by low-current implantation. The morphology shown in figure 4(a) seems like a fractal pattern and this is confirmed by fractal dimension measurements. It was calculated that an average fractal dimension of the pattern was about 1.90 ± 0.06, which was quite close to that of the percolation network. This probably explains why the sheet resistivity of the high-current implanted samples was reduced quite a lot from that of the Ge wafers and the low-current implanted samples, though the PdGe phase did not form a uniform layer on the wafer surface.

As we know, the MEVVA ion source was implanted with a pulsed beam. In each pulse, while implanting, the pulsed beam provides a certain number of energetic Pd ions lanching into the surface layer of Ge in a short time as well as heating the Ge substrate simultaneously. The percolation structure seen in figure 4(a) can be viewed to be formed as follows. After implantation to a certain dose, though the overall Pd concentration in the Ge surface layer did not reach an exact stoichiometry of Pd/Ge = 1:1, in some local regions, induced by compositional fluctuation, it can be high enough to nuclei some PdGe seeds. Further launching of the Pd atoms into Ge increased the number of PdGe grains as well as leading some grains to grow. Statistically, there were some big grains, which did not move, while small ones moved laterally, though the movement was very limited in the solid state. When the implantation was going on, some grains became inter-connected, resulting in the formation of the above observed fractal structure. The formation of the percolation network was responsible for the reduced sheet resistivity of the Ge wafers, though the overall Pd concentration in the implanted layer was still far below 50 at.%.

4. Concluding remarks

The equilibrium PdGe phase can be synthesized by a single-step MEVVA Pd-ion implantation into Ge wafers under appropriate experimental conditions. Interestingly, in the case of high-current implantation, the formed PdGe grains organized themselves in a fractal pattern like a percolation network with a dimension of 1.90 and the sheet resistivity of the wafer was therefore reduced significantly to 59 $\Omega\,\square^{-1}$.

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