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A preliminary study of the formation of WSi_2 by high-current W ion implantation

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Abstract. Two differently structured WSi_2 phases were formed by direct W ion implantation, for the first time, into silicon wafers using a metal vapour vacuum arc ion source. Implantation of W ions was conducted with an extract voltage of 40 kV, various beam densities from 50 to 115 $\mu A\ cm^{-2}$ and a fixed dose of $5 \times 10^{17}\ cm^{-2}$. It was found that the formation of WSi_2 with either a hexagonal or a tetragonal structure depended on the ion current density. The temperature rise caused by beam heating and the beam-striking time related to the dose were calculated, and they were responsible for the formation and evolution related to the differently structured WSi_2 phases.

1. Introduction

Metal silicide thin films, which have been studied for more than 20 years because of their potential application in ultra-large-scale integration (ULSI), have been generally fabricated by means of thermally induced or ion-mixing-induced reaction [1, 2] between deposited thin metal films and silicon single crystals. Of the metal silicides, tungsten disilicide is very attractive because of its relatively low resistivity, high thermal stability and unique oxidation capability [3–5].

The properties of WSi_2 films on silicon wafers depend on the different crystalline structures of WSi_2, i.e. the hexagonal structure (C40 with $a = 4.164$ Å and $c = 6.414$ Å) usually formed by annealing in the temperature range 400–600 °C or the tetragonal structure (C11b with $a = 3.211$ Å and $c = 7.869$ Å) formed by annealing at a temperature of 700 °C or higher [6, 7].

Ion beam synthesis is a promising technique for fabricating silicides, e.g. continuous buried $CoSi_2$ [8, 9], α-$FeSi_2$ and β-$FeSi_2$ [10, 11] layers have been formed by high-dose Co and Fe ion implantation into Si single crystals at an elevated Si wafer temperature and post-annealing. In contrast with the conventional ion beam synthesis techniques previously employed, a high current density of various metal ions can be readily extracted from a newly invented metal vapour vacuum arc (MEVVA) ion source [12]. If MEVVA ion implantation were employed to form various metal silicides, the high-current ion beam would certainly heat the Si wafers up to high temperatures and reach the temperatures required for forming various metal silicides by adjusting the current density and dose. Apparently, the MEVVA source provides a possible manufacturing technique which requires only a single implantation step. The feasibility of the MEVVA technique has been verified by our previous study in forming the C54 $TiSi_2$ phase with a very low resistivity by direct Ti ion implantation [13]. In

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this paper, we report the preliminary results of the formation of WSi_2 fabricated by direct high-current W ion implantation into Si(111) wafers.

2. Experimental procedure

Before loading onto a steel sample holder, the p-type Si(111) wafers with a resistivity of 8–13 Ω cm were cleaned by a routine chemical procedure and then dipped in a dilute HF solution, followed by a rinse in deionized water. The samples were not deliberately cooled during implantation which was carried out in a MEVVA source implanter with a vacuum level of better than 5×10^{-3} Pa. Various current densities of W ion implantation, ranging from 50 to 115 μA cm^{-2}, were performed at an extract voltage of 40 kV and a dose of 5×10^{17} W cm^{-2}. The ion beam consisted of 8% W^+, 34% W^{2+}, 36% W^{3+}, 19% W^{4+} and 3% W^{5+}. The samples were implanted with a tilt angle of 7° to avoid the channelling effect.

X-ray diffraction (XRD) measurements were conducted using a D/max-RB diffractometer with a Cu radiation source operated at 40 kV and 80 mA. The implanted W ion profiles were determined by Rutherford backscattering spectrometry (RBS) at a 165° scattering angle with 2.1 MeV He particles.

3. Results and discussion

3.1. Phase formation of WSi_2

In the sample implanted by W ions with a current density of 50 μA cm^{-2}, no silicide can be observed by XRD. The XRD spectra of two differently structured WSi_2 phases obtained in the samples implanted with W ions at various current densities are shown in figure 1. When the current density was increased to 65 μA cm^{-2}, a peak of $d = 2.154$ Å appeared (figure 1(*a*)), corresponding to the (111) line of hexagonal WSi_2 [7]. Figure 1(*b*) reveals that the hexagonal phase of WSi_2 is completely formed in the sample implanted with W ions at a current density of 75 μA cm^{-2}. As can be seen from figure 1(*c*), the hexagonal-to-tetragonal phase transformation began to take place when the ion current density was increased to 90 μA cm^{-2}. On implantation at an ion current density of 115 μA cm^{-2}, the tetragonal WSi_2 phase was formed, which accorded with [14], and coexisted with its hexagonal counterpart (figure 1(*d*)).

In previous reports the formation of hexagonal WSi_2 was anticipated on lower-temperature annealing, while the tetragonal structure would be formed at higher temperatures. It had been deduced that a temperature of the order of 550 °C was necessary to initiate the transition from hexagonal WSi_2 to the tetragonal WSi_2 [7] and that the tetragonal phase was the only phase present beyond 700 °C, demonstrated by other techniques [6, 7, 15]. In our case, changing the ion current density in MEVVA source implantation corresponds to varying the effective annealing temperature, which in turn induces the formation of WSi_2 with the corresponding structures. The quantitative calculation of the temperature rise versus ion current density is discussed later in section 3.3.

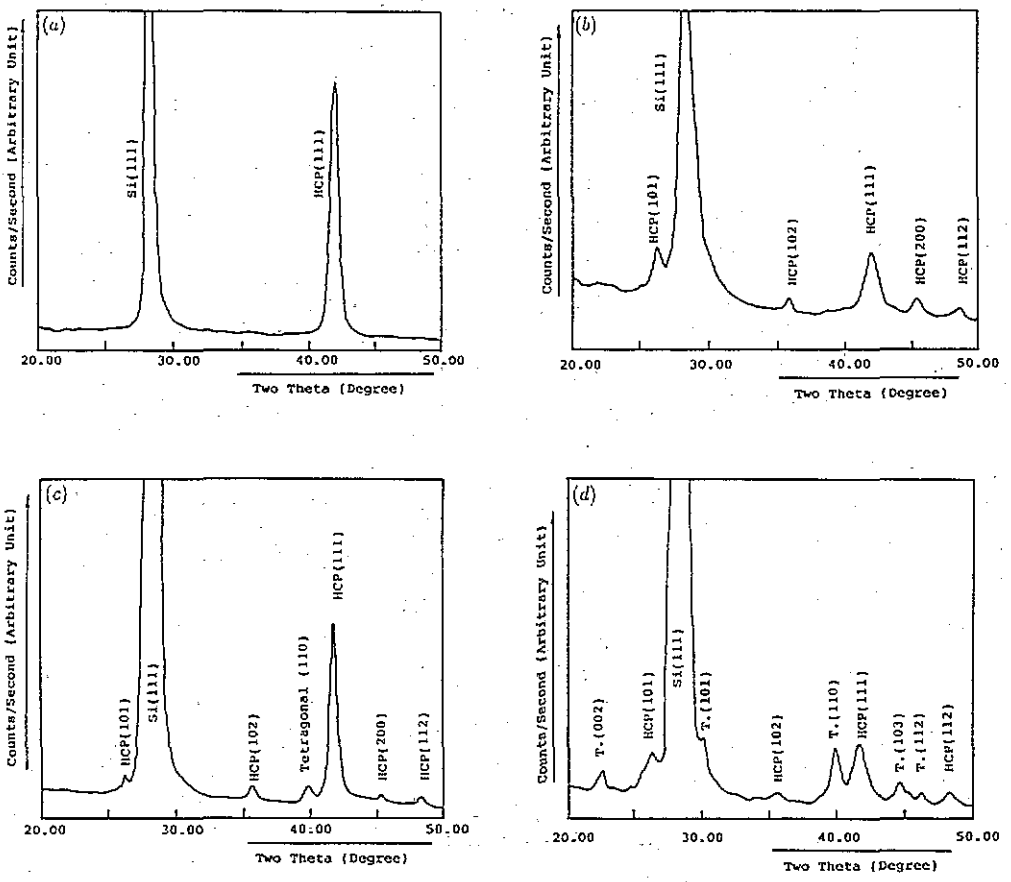

Figure 1. XRD spectra of Si(111) samples implanted with W ions to a dose of 5×10^{17} cm^{-2} at various current densities: (*a*) 65 μA cm^{-2}; (*b*) 75 μA cm^{-2}; (*c*) 90 μA cm^{-2}; (*d*) 115 μA cm^{-2}.

3.2. Diffusion of W ions in silicon

The two Rutherford backscattering spectra in figure 2 were obtained from the samples implanted with W ions at two current densities of 65 and 90 μA cm^{-2} at a fixed dose of 5×10^{17} cm^{-2}. The spectrum in figure 2(*a*) for the sample implanted with W ions at a current density of 65 μA cm^{-2} shows that a relatively sharp silicide layer with an average stoichiometry of W:Si = 1:2.33 had been formed at the surface layer, 300 Å thick. When the current density was increased to 90 μA cm^{-2}, the corresponding spectrum in figure 2(*b*) demonstrates that the W ions had diffused considerably into the depth of Si and the peak W concentration reached an average stoichiometry of W:Si = 1:3.4 within a 300 Å flat distribution and a 400 Å enhanced diffusion layer. The higher the current density, the more W ion diffusion takes place. The Rutherford backscattering spectrum in figure 3 reveals that the W profile extended markedly to a depth of 1000 Å when the current density was increased to 115 μA cm^{-2}. The stoichiometry of W:Si in the implanted layer was 1:4 and the Si concentration increased deeper into the layer. However, for all the above implanted samples, XRD detected only WSi_2 phases and no other compounds. These results meant that the WSi_2 phase formed directly after implantation was not uniform.

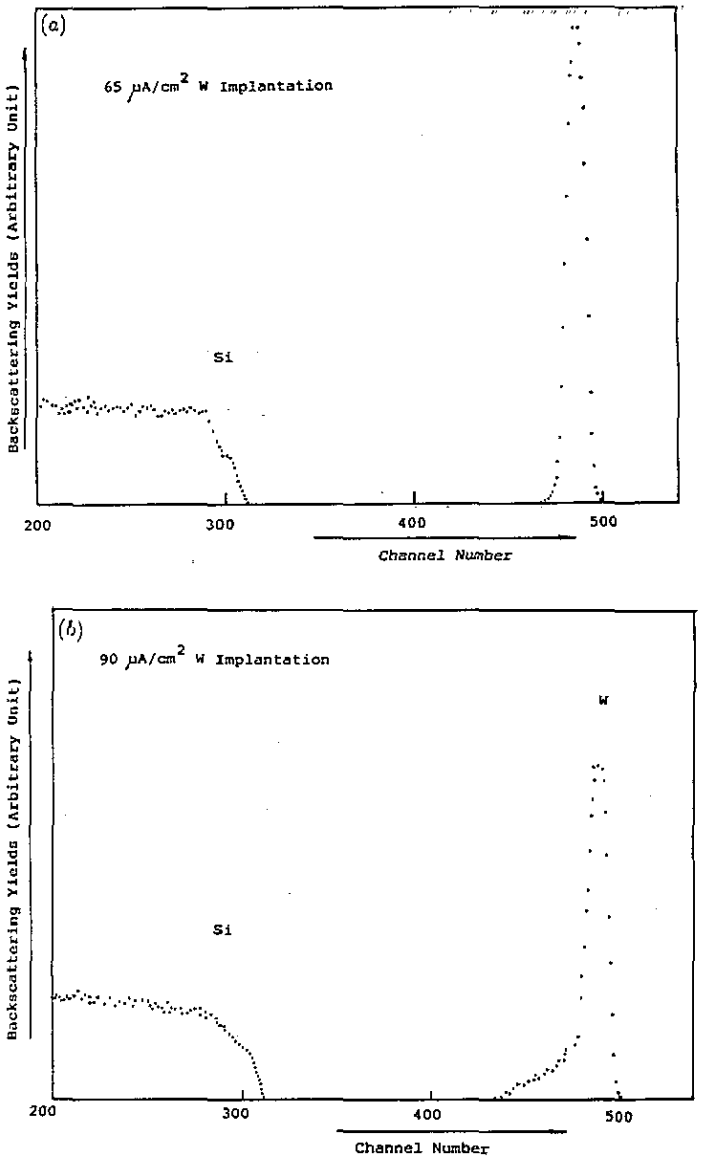

Figure 2. Rutherford backscattering spectra of Si(111) samples implanted with W ions to a dose of 5×10^{17} cm^{-2} at two current densities: (*a*) 65 μA cm^{-2}; (*b*) 90 μA cm^{-2}.

3.3. Beam-heating effect in MEVVA implantation

Both the x-ray and RBS results indicate that the beam-heating effect plays an important role in determining the uniformity and the crystalline structure of the WSi_2 formed. The instantaneous temperature rise under ion implantation can be calculated using the expression of Wittkower and Hirvonen [16]:

$$\Delta T(t) = T(t) - T_s = 2P\cos\theta\sqrt{t/k\rho C_p}\ (^\circ\mathrm{C}) \tag{1}$$

where $T(t)$ (°C) is the instantaneous temperature of the sample surface, T_s (°C) the average temperature, P (W cm^{-2}) the instantaneous power density of the ion beam, k

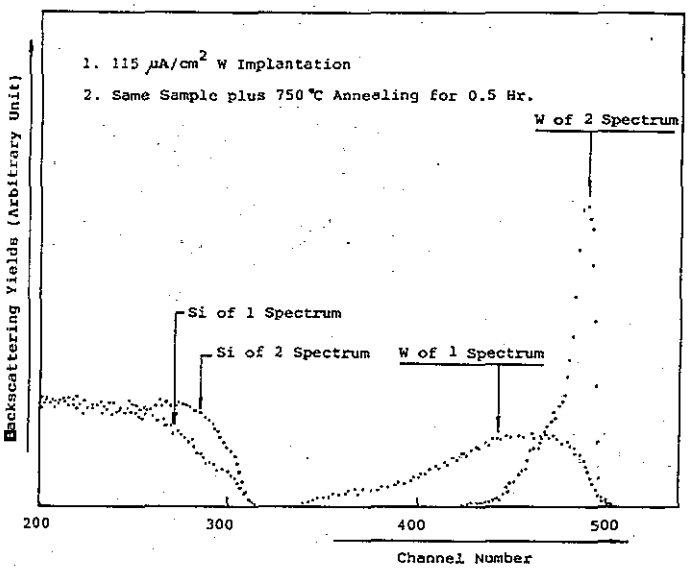

Figure 3. Rutherford backscattering spectra of an Si(111) sample implanted with W ions to a dose of 5×10^{17} cm^{-2} at a current density of 115 μA cm^{-2} before (spectrum 1) and after annealing (spectrum 2).

(W cm^{-1} °C^{-1}) the thermal conductivity of the material being implanted, C_p (W s g^{-1} °C^{-1}) the specific heat of the material being implanted, ρ (g cm^{-3}) the density of the material being implanted, θ (deg) the tilt angle of implantation and t (s) the beam striking time.

Under our experimental condition, θ is 7°, and the values of k and C_p for Si are 0.84 W cm^{-1} °C^{-1} and 1.58 W s cm^{-3} °C^{-1}, respectively. Equation (1) becomes

$$\Delta T(t) = 1.47J\sqrt{t} \tag{2}$$

where J (μA cm^{-2}) is the instantaneous ion beam current density and t (min) the beam-striking time.

In order to illustrate explicitly the relationship between the crystalline structure of WSi_2 and the beam-heating effect, the details of WSi_2 phases and the beam-striking times versus various current densities are listed in table 1. In addition, five $\Delta T(t)$ versus t curves are given in figure 4 to show the temperature rise process during implantation. For current densities of 65 and 75 μA cm^{-2}, the temperature rise is in the same range 400–600 °C, and the beam-striking times are 22 min and 17 min for figure 4, curve 2 and curve 3, respectively. In both cases, the observation of only a hexagonal phase after implantation coincides with the previously reported results [6]. When the current density is increased to 90 μA cm^{-2}, the beam-striking time is 10 min in the temperature range 600–700 °C (figure 4, curve 4), which results in the hexagonal-to-tetragonal phase transition as shown by the (110) line for tetragonal WSi_2 shown in figure 1(*d*). This result is also in accordance with previous reports.

Unlike the formation of hexagonal WSi_2 in the temperature range 400–550 °C as reported previously, no tungsten silicide was detected when implanting W ions at a current density of 50 μA cm^{-2}, which corresponded to a temperature rise of between 400 and 540 °C (figure 4, curve 1). Also, the hexagonal phase remained even when the current density was increased to 115 μA cm^{-2}, which caused the temperature rise to be above 700 °C (figure 4,

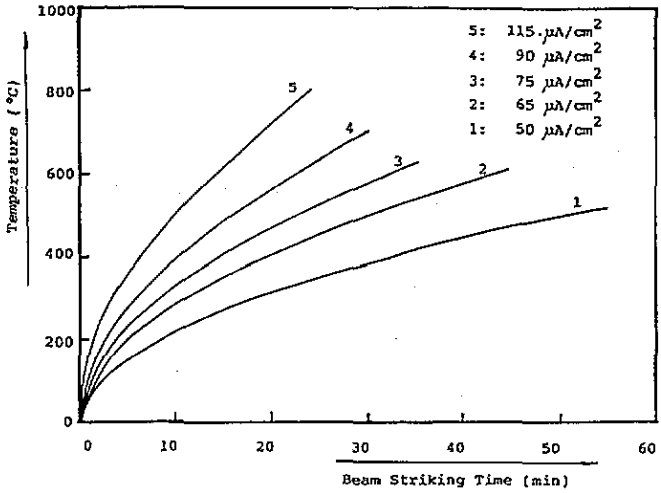

Figure 4. Dependence of the temperature rise on beam-striking time of W ions implanted into Si(111) at various current densities.

Table 1. Different phases of WSi_2 identified by x-ray diffraction for various W ion current densities: H, hexagonal structure; T, tetragonal structure.

Phases for the following j and t				
50 μA cm^{-2} 54 min	65 μA cm^{-2} 43 min	75 μA cm^{-2} 36 min	90 μA cm^{-2} 31 min	115 μA cm^{-2} 24 min
None	H(111)	H(101)	H(101)	H(101)
		H(102)	H(102)	H(102)
		H(111)	H(111)	H(111)
		H(200)	H(200)	H(112)
		H(112)	H(112)	T(002)
			T(110)	T(101)
				T(110)
				T(103)
				T(112)

curve 5). These results can be explained by an insufficient beam-striking time, which was limited by a fixed dose of 5×10^{17} cm^{-2}. Naturally, the growth kinetic conditions for metal silicide formation relate to not only the temperature but also the time of interaction between metal and silicon and, in the implantation case, depend on the ion current density as well as the total implantation dose. The beam-striking times for the above two samples were only 25 min and 7 min, respectively, which were too short for the corresponding phase formation or transition to be completed.

From the above explanation in terms of the beam effect and the RBS results, it is necessary to increase the reactive time between W and Si so that a well grown tetragonal WSi_2 layer with a relatively sharp interface may be formed. For the sample implanted with W ions at a current density of 115 μA cm^{-2}, post-annealing was conducted at 750 °C for 0.5 h in a furnace with a vacuum level of 3×10^{-3} Pa. The Rutherford backscattering spectrum 2 in figure 3 shows that, after annealing, a relatively sharp WSi_2 layer was formed. Meanwhile, as can be seen in the XRD pattern in figure 5, only the diffraction lines from tetragonal WSi_2 are shown in the annealed sample, indicating that the hexagonal-to-

tetragonal transition was complete. This result can be attributed to an additional reaction between W and Si caused by post-annealing. It is believed that this can also be done by adding a certain amount of implantation dose corresponding to an increase in the beam-striking time. In other words, for high-current ion implantation, not only the beam current density but also the implantation dose should be adjusted for the formation of a uniform metal silicide layer with a relatively sharp interface. The related research on various metal–silicon systems is now currently being undertaken by this group.

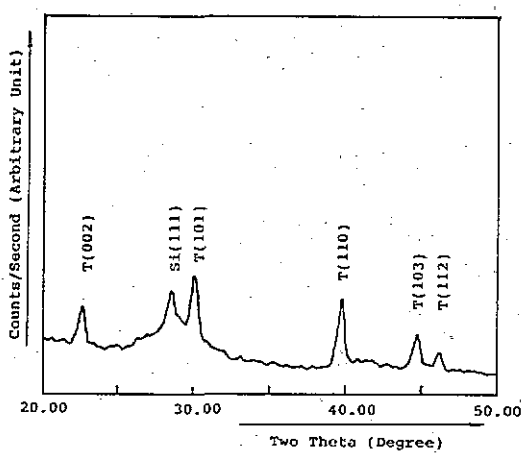

Figure 5. XRD spectrum of an Si(111) sample implanted with W ions at a current density of 115 μA cm^{-2} to a dose of 5×10^{17} cm^{-2} and annealed for 30 min at 750 °C.

In summary, two differently structured WSi_2 phases can be formed by direct implantation employing the MEVVA ion source. The phase formation of WSi_2 with either a hexagonal or a tetragonal structure closely relates to the ion current density. The calculation of the temperature rise suggests that an effective annealing process with increasing temperature occurs simultaneously during implantation; this is responsible for forming the WSi_2 phases. The above results show the possibility of the application of the MEVVA source in ULSI research and development; however, many more studies are certainly required.

Acknowledgments

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