Extended Abstracts of the 1994 International Conference on Solid State Devices and Materials, Yokohama, 1994, pp. 625-627

Low-Temperature (400°C) W-Silicide Formation by High-Energy Xe^+-Ion Beam Irradiation

Toru Yamaguchi, Jyoji Nakata and Katsumi Murase

NTT LSI Laboratories

3-1, Morinosato Wakamiya, Atsugi-shi, Kanagawa-ken, 243-01, Japan

Uniform and stoichiometric WSi_2 layers can be formed by high-energy Xe^+ irradiation into both W-deposited and high-dose W^+-implanted samples at 400°C. The formation of these silicides was studied by Rutherford backscattering spectroscopy and cross-sectional transmission electron microscopy. The interface and the surface of WSi_2 layers are much smoother and abrupter than those of thermally formed W-silicide layers. For low-dose W^+-implanted samples, crowding of W atoms to the surface was induced by Xe^+ irradiation. This indicates the feasibility of forming nm-order-thick W-silicide by combining low-energy W^+-implantation and subsequent high-energy Xe^+ irradiation.

I. INTRODUCTION

High-energy heavy-ion-beam irradiation (HHBI) is a powerful technique for surface modification at low temperatures. For example, an amorphous Si layer on a crystalline Si substrate can be crystallized epitaxially by HHBI at a temperature as low as 300°C [1]. In addition, HHBI is characterized by its high uniformity and controllability. Therefore, it is expected that nm-order-thick compounds can be formed by adopting the HHBI technique. However, there are few reports on compound formation by HHBI at low temperatures [2–4]. In this paper, we show, for the first time, W-silicide formation by irradiating W-deposited Si wafers and W^+-implanted ones with 1-Mev Xe^+ ions, and discuss the applicability of high-energy Xe^+ irradiation to nm-order-thick W-silicide formation.

II. EXPERIMENTAL

Tungsten films about 20 nm thick were formed by chemical vapor deposition on (100) Si wafers at 330°C. Then, a part of a wafer was irradiated through a 2 × 2 cm^2 mask-window with 1-MeV Xe^+ ions to a dose of 1×10^{15} cm^{-2} at 400°C. For thin W-silicide formation, samples were also prepared by 30-keV W^+ implantation at room temperature followed by 1-MeV Xe^+ irradiation at 400°C. The dose was 1.9×10^{16} (low dose) or 1.4×10^{17} cm^{-2} (high dose) for W^+ implantation, while it was varied from 2×10^{14} to 5×10^{15} cm^{-2} for Xe^+ irradiation. The W profiles and compositions of the formed compound layers were determined by Rutherford backscattering spectroscopy (RBS). Microstructures were observed with a cross-sectional transmission electron microscope (XTEM).

III. RESULTS AND DISCUSSION

First, we investigated W-silicide formation for W-deposited samples. An abrupt and stoichiometric WSi_2 layer (23 nm) was formed near the W-Si interface as a result of Xe^+ irradiation at 400°C, as evidenced by the RBS random spectrum (solid line) shown in Fig. 1. The WSi_2 layer was found to grow further towards the surface with increasing Xe^+ dose. For comparison, some samples were subjected to thermal annealing. As shown in Fig. 1, annealing at 700°C results only in diffusion of W atoms, and does not lead to stoichiometric W-silicide formation. For a sample annealed at 800°C, although the WSi_2 phase is created, Si-rich W-silicide is also formed and penetrates deeper into the substrate.

Figure 2 shows XTEM micrographs of the same samples in Fig. 1. Both the interface and the surface of W-silicide formed by Xe^+ irradiation are flat and smooth, while those of W-silicide formed by thermal annealing are irregular and rough.

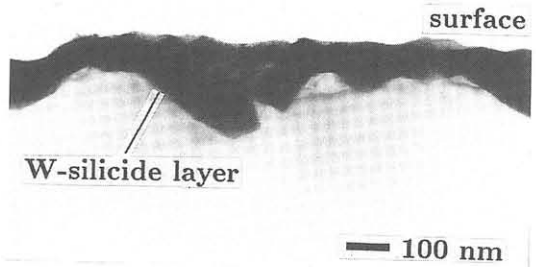
From Figs. 1 and 2, it is clear that ion-beam-induced W-silicide is superior to thermally formed one in terms of reducing formation temperature, obtaining the stoichiometric phase, and smoothing the interface and surface. Therefore, it is expected that nm-order-thick W-silicide layers with an abrupt interface can be formed by HHBI at low temperatures.

Next, we investigated W-silicide formation for high-dose W-implanted samples. The dependence of the W profile on the Xe^+ dose is shown in Fig. 3 for the high-dose W^+-implanted samples. The as-implanted W profile is not gaussian but flat-top like because sputtering occurs during low-energy high-dose implantation, which was confirmed from highly

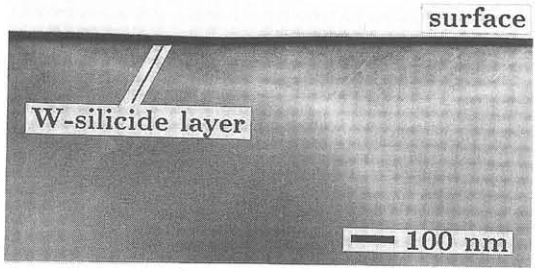
resolved RBS random spectra obtained by the glancing angle RBS method (not shown here). The concentration ratio of W to Si in the as-implanted layer is about 3 : 1. As in the case of W-deposited samples, the WSi_2 layer grew toward the surface with increasing Xe^+ dose; a 40-nm WSi_2 layer formed with a 1×10^{15} cm^{-2} dose.

Figure 4 shows the number Q_{Si} of intermixed Si atoms as a function of Xe^+ dose. For W^+-implanted samples, Q_{Si} increases proportionally to Xe^+ dose at Xe^+ doses below 5×10^{14} cm^{-2}. However, Q_{Si} becomes saturated at Xe^+ doses above 7×10^{14} cm^{-2} because all W atoms are consumed to form the WSi_2 phase and further intermixing is suppressed. For W-deposited samples on the other hand, Q_{Si} is not saturated because W atoms remain to be intermixed. As seen from Fig. 4, before W-silicide formation becomes saturated, Q_{Si} for W^+-implanted samples is 1.5 times as large as Q_{Si} for W-deposited ones. This indicates that intermixing occurs more effectively for W^+-implanted samples than for W-deposited ones.

Finally, the possibility of the nm-order-thick W-silicide formation by HHBI was investigated for low-dose W^+-implanted samples. The dependence of the RBS channeling spectrum on the Xe^+ dose is shown in Fig. 5. The W profile becomes narrower and shifts towards the surface as Xe^+ dose increases, which is suitable for fabricating nm-order-thick W-silicide layers.When Xe^+ dose is 5×10^{15} cm^{-2}, for example, the full width at half maximum of the W profile reduced from 17 nm to 14 nm, and the peak position of the W profile shifted to the surface by 11 nm (Fig. 5(a)).



(a)annealing at 700°C



(b)Xe^+ irradiation at 400°C

Figure 2. XTEM micrograph of the samples in Fig. 1.

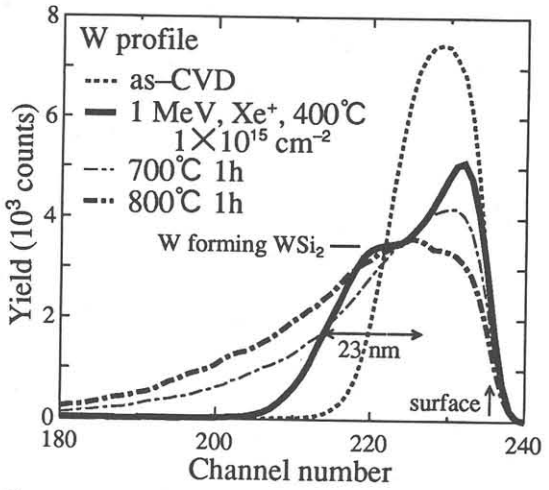


Figure 1. RBS random spectra of a 20 nm thick W film on Si substrate before and after Xe^+ irradiation and thermal annealing.

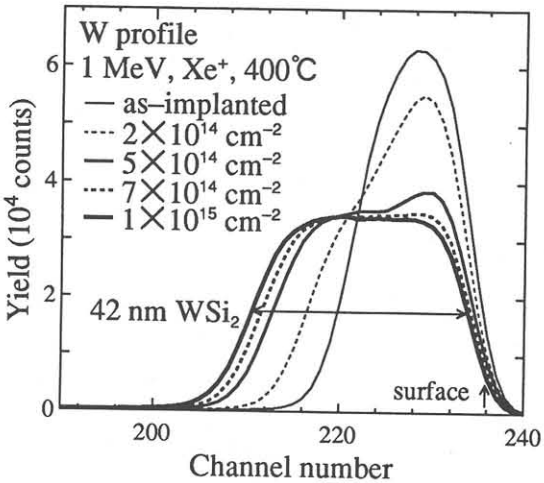


Figure 3. RBS random spectra of the high-dose W^+-implanted samples before and after Xe^+ irradiation.

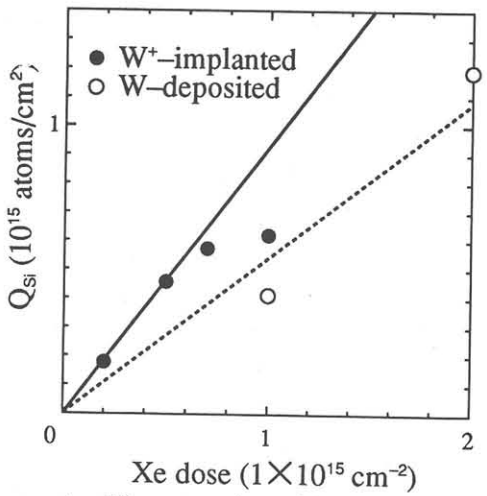


Figure 4. The quantity of intermixed Si atoms versus the Xe^+ dose.

At the same time, the W peak height increased as a result of profile narrowing. However, in this case, the W peak height did not reach a concentration high enough to form the WSi_2 phase, since the W^+ dose was still insufficient. Incidentally, it is pointed out here that amorphous Si layers formed by low-dose W^+ implantation are crystallized epitaxially for 19 nm by 2×10^{15} cm^{-2} Xe^+ dose, and 22 nm by 5×10^{15} cm^{-2} dose at a temperature as low as 400°C (Fig. 5(b)).

Figure 6 shows XTEM micrographs for the same samples in Fig. 5. In the W^+-implanted sample not subjected to Xe^+ irradiation (Fig. 6(a)), the W^+-implanted layer is observed around 20 nm deep and a heavily damaged region is formed deeper than 150 nm below the surface. Xe^+ irradiation recrystallizes this damaged region completely and forms a very thin composite layer of W and Si near the surface (Fig. 6(b)).

Results in Fig. 5 indicate that WSi_2 is not formed under low-dose W^+ implantation. However, results in Figs. 5 and 6 together with those for high-dose W^+-implantation suggest that nm-order-thick W-silicide can be formed by low-energy W^+-implantation with an optimum W dose coupled with subsequent low-temperature high-energy Xe^+-irradiation.

IV. CONCLUSION

We have studied forming W-silicide by 1-MeV Xe^+ irradiation at 400°C. A stoichiometric WSi_2 layer is formed by irradiating a W-deposited sample with Xe^+ ions. The interface and surface of WSi_2 layer are much smoother and abrupter than those of thermally formed W-silicide layers. When a W^+-implanted sample is irradiated with 1-MeV Xe^+ ions, a WSi_2 layer is formed more effectively than for a W-deposited sample; The number of Si atoms intermixed with W atoms for the W^+-implanted sample is 1.5 times as large as that for the W-deposited sample. In addition, we showed the feasibility of forming nm-order-thick W-silicide layers by combining low-energy W^+ implantation with subsequent HHBI.

ACKNOWLEDGMENTS

We would like to thank Dr. Katsutoshi Izumi for his encouragement throughout this work. We are also grateful to Hiromu Ishii, Dr. Toshihiko Kosugi and Torao Saito for sample preparations.

[1] J. Nakata, *Phys. Rev.* **B43** (1991) 14643.

[2] M. C. Ridgway, R. G. Elliman and J. S. Williams, *Mat. Res. Soc. Symp. Proc.* **157** (1990) 131.

[3] A. Golanski, W. H. Christie, M. D. Galloway, J. L. Park, S. J. Pennycook, D. B. Poker, J. L. Moore, H. E. Harmon and C. W. White, *Nucl. Instr. and Meth.* **B59/60** (1991) 444.

[4] A. M. Ektessabi and K. Ogino, *Proc. 1st Meeting on IESJ'92 Tokyo* (1992) 205.

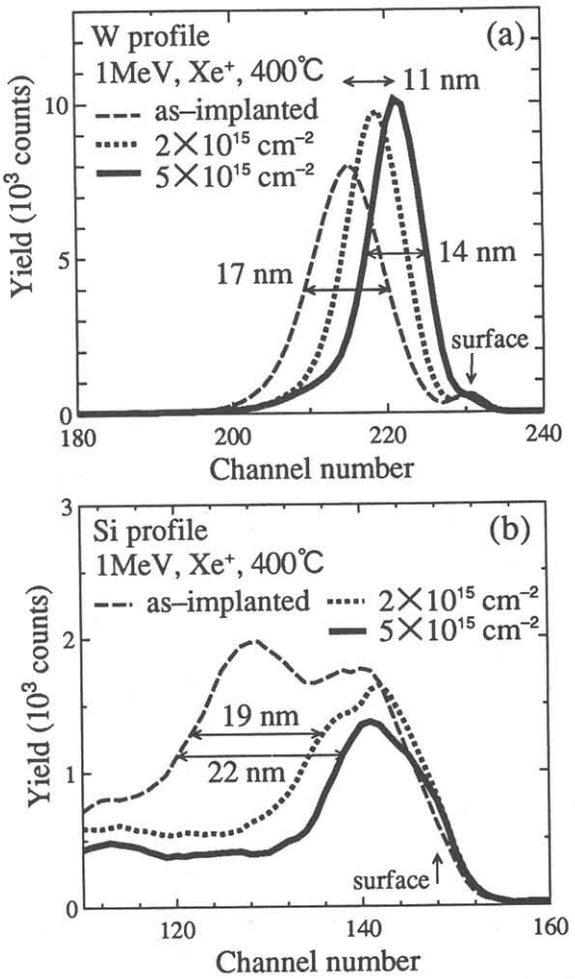
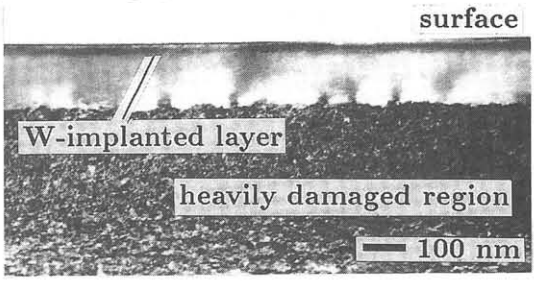
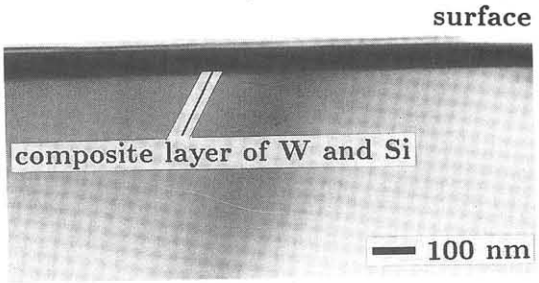


Figure 5. Irradiation dose dependence of the RBS [110]-channeling spectra.



(a)as-implanted



(b)Xe^+ irradiation to a dose of 5×10^{15} cm^{-2}

Figure 6. XTEM micrographs of the samples in Fig 5