Focused Ion Beam Induced Formation of Pd Silicide

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Abstract

Focused ion beam (FIB) irradiation of a thin Pd silicide layer deposited on a Si substrate was carried out and studied using an in-situ transmission electron microscope (in-situ TEM). Square areas on sides of 4 by 4 μm were patterned at room temperature with a 25keV Ga^+-FIB attached to the TEM. The structural changes of the films after the FIB irradiation shows an uniform milling; sputtering of the Pd silicide layer and introducing the radiation damage to the Si substrate. Subsequent annealing at 673 K for 15 minutes results in the formation of Pd silicide islands far outside the FIB irradiated area, but this island formation is suppressed and the silicide film remained near the irradiated area. Energy dispersive X-ray spectroscopy (EDS) indicates that the content of Pd in the islands is larger than that in the film. Selected area diffraction (SAD) patterns and the corresponding dark field images of the remaining film imply the partial transformation of the Pd silicide to Si rich silicide. The beam broadening of the FIB tail is concluded to have a close relationship with the morphology changes in Pd silicide.

1. Introduction

Focused ion beam (FIB) is becoming an effective tool in the formation of submicron devices, in which local etching, deposition, implantation and patterning of materials have been conducted to the substrates [1,2]. Minimum spot size of about 0.1 μm and large current density of about -A/cm^2 of the FIB make it possible to perform the maskless implantation and lithography. Besides several advantages of the FIB, it has a few disadvantages such as production of radiation damages to the target materials and the subsequent structural changes. Ion exposure to the sample usually causes defects production, amorphization and ion-mixing in materials. Ion beams which are finely adjusted and focused generally provide inhomogeneous spatial distribution of ion flux which induce unexpected reactions in the target materials. The beam profile of the FIB is becoming a problem during maskless implantation into sensitive materials. The current density distribution of FIB is generally acknowledged to have a central Gaussian peak accompanied by a long tail [3,4]. This tail, combined with radiation damage, may cause undesirable reaction to a part of the target material where the fabrication is not expected.

A 200 keV TEM, incorporating a 25 keV Ga-FIB (FIB/TEM) [5,6], was developed to characterize the structural changes of thin semiconductor substrates caused by the FIB irradiation. This equipment enables the FIB irradiation and the simultaneous observation so that one can directly observe the radiation damage or beam broadening effects on the sample, excluding the artifacts often induced in TEM samples with a conventional preparation process. Ni silicide films on a (111) Si substrate have already been micromilled and studied with the FIB/TEM [7,8]. The results showed precipitation of Ni rich silicide in and near the FIB irradiated area in the case of a Ni_2Si film and fragmentation of the silicide in the case of a $NiSi_2$ film.

In this study, the micromilling of a Pd silicide/Si bi-layer with the FIB/TEM is performed to investigate the structural changes caused by FIB irradiation and by post-irradiation annealing. Pd is adopted because epitaxial Pd_2Si also has little mismatch with Si like epitaxial $NiSi_2$. The effect of FIB irradiation on the formation of Pd silicide islands in terms of beam broadening effects is discussed.

2. Experimental

Fig. 1 shows a schematic drawing of the Ga^+-FIB system attached to the objective lens column of a TEM (JEM-200CX) with an incident beam angle of 35° with respect to the electron beam and with a working distance of 100 mm. FIB irradiation was carried out at room temperature. The FIB energy is 25 keV with a beam diameter of about 0.2μm and a beam current of about 80 pA. Blanking and drawing of the ion beam are computer-

controlled. 4 by 4 μm squares were patterned at a constant scanning speed of 1.5 μm/s. This corresponds to a Ga ion dose of 1.66×10^{17} ions/cm^2. The FIB irradiation is carried out one time on a small part of the sample where large unirradiated area is remained.

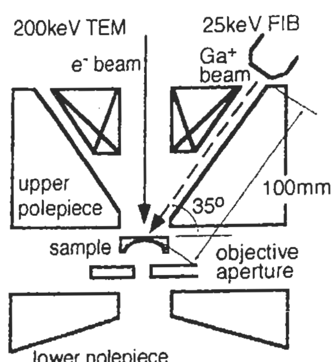

Fig. 1 Schematic diagram of the objective lens column of the TEM (JEM-200CX) equipped with an in-situ 25 keV Ga^+-FIB

Samples were prepared from 5~10 ohm cm B doped Si (111) wafers. After Ar ion thinning, they were loaded into an ultra-high vacuum chamber (base pressure of 2×10^{-8} Pa) and annealed at 1173K for 30 minutes to remove the surface amorphous layer. Pd was deposited onto the samples by electron beam evaporation to a thickness of 2 nm at a rate of 0.01 nm/s at 573K followed by in-situ annealing at 673 K for 15 minutes. TEM observation of as-deposited samples indicates the formation of Pd/Pd_2Si mixed phase. Pd_2Si has a hexagonal structure with lattice parameter of 0.65 and 0.34 nm for the a- and c-axes, respectively. Although the Pd silicide film was not uniform, the average thickness of the silicide layer was estimated to be about 3 nm. FIB irradiation caused the degradation of the sample film. After the FIB irradiation, the samples were annealed at 673K for 15 minutes in a vacuum chamber with infrared lights in order to improve the film quality. Morphological changes of silicide around the irradiated area of the sample were analyzed with the TEM and with energy disperse X-ray spectroscopy (EDS) at a voltage of 200kV.

3. Results and Discussion

The beam profile of the FIB has been measured by a spot exposure of the FIB on a (111) Si TEM sample [10]. This point irradiation for 1500 seconds resulted in making a hole on the sample and the TEM images were recorded simultaneously on a video tape throughout the irradiation. Astigmatism of the FIB has been carefully compensated by a stigmator to produce an isotropic beam profile. The area of the hole dug in the sample were measured and plotted against exposure time as solid circles in Fig. 2. Since the energy required to sputter out a certain number of silicon atoms from the sample is fixed at specific beam condition, the size of the milled area at particular exposure time is proportional to the total amount of Ga ion. Thus it follows that the fitted curve (dashed line) roughly represents the current distribution of the FIB. Contrary to a Gaussian profile supported by other researchers [3-4,9], our fitting curve has an exponential profile, and describes the shape of the beam with a sharp peak and a long tail which spreads about

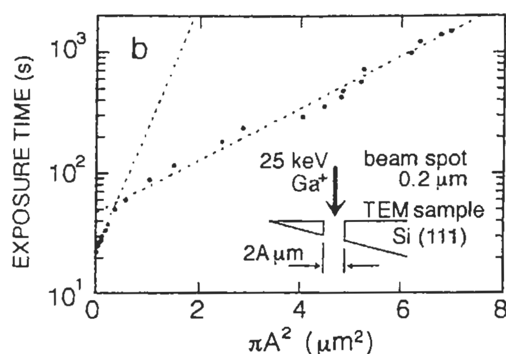

Fig. 2 Fits to FIB exposure time vs. the area size of the milled whole showing peak region and long tail region.

several μm.

Fig. 3 shows TEM micrographs of a Pd silicide layer as-irradiated by the FIB over a 4 by 4 μm-square. Fig. 3a shows a bright-field image of the FIB irradiated area. The boundary between the irradiated and unirradiated area is recognized. No morphology change was observed in the unirradiated area as shown in Fig. 3b and its SAD pattern in Fig. 3c. On the other hand, a TEM image inside the irradiated area (Fig. 3d) shows a drastic change of the microstructure from a crystal/amorphous mixed phase to a heavily damaged state. This is also observed in the corresponding SAD pattern (Fig. 3e). Since the thickness of the Pd silicide film is about 3 nm, most of the silicide is considered to be sputtered off and the remaining Si substrate changes to a damaged state.

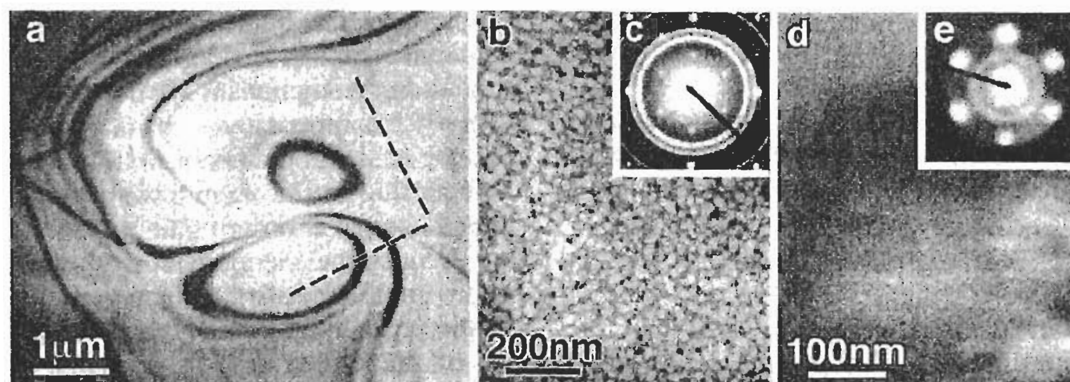

Fig. 3 TEM micrographs of the Pd silicide thin film after the FIB irradiation. (a) a bright-field image of the FIB irradiated area before annealing. Dashed lines indicate the irradiated square edge. (b) The magnified image and (c) corresponding SAD pattern of the unirradiated part of the sample, show great difference from (d) the magnified image of the irradiated part and (e) its SAD pattern.

The post-irradiation annealing was performed at 673K for 15 minutes to improve the silicide film quality and the resultant image and the corresponding SAD pattern are shown in Fig. 4a and b, respectively. The improvement of film quality is seen as polycrystallization of the irradiated area in the image. But the radiation damage in the area still exists, which is confirmed by the Debye-rings in the SAD pattern.

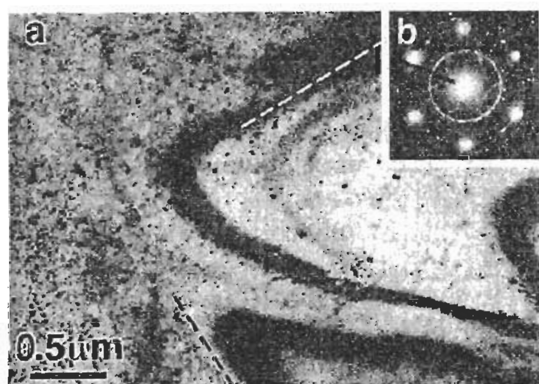

Fig. 4 Pd silicide film after annealing. (a) A bright-field image showing grains and defects. Dashed lines indicate the irradiated square edge. (b) Its SAD pattern.

The morphological changes of the silicide in the unirradiated area are shown in Fig. 5. Fig. 5a represents the image taken about 10 μm away from the irradiated square edge. The image is similar to the image of Pd silicide film before annealing. But the corresponding SAD pattern in Fig. 5b displays extra three symmetric spots surrounding Pd_2Si (110) spots, which was not observed before annealing. Dark field microscopy suggests that these spots are not from Pd_2Si film, but from another phase. This indicates the partial transformation of the Pd_2Si into other phases, probably into PdSi. Fig. 5c shows the image taken about 20 μm away from the irradiated square edge. Most of the silicide forms islands and little film is left in the figure. A SAD pattern taken from the island (Fig. 5d) suggests that the island consists of one silicide phase, possibly Pd_2Si. As the distance from the irradiated square edge increases from 10 to 20 μm, the coverage of the film area decreases and the size and number of the islands increases.

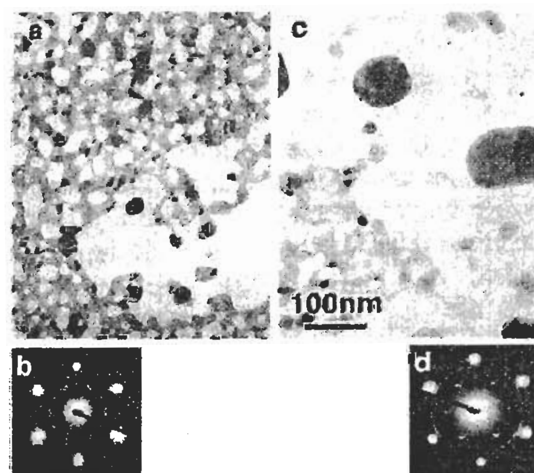

Fig. 5 The gradual change of the Pd silicide morphology. (a) A image of the Pd silicide film taken at a place 10 μm away from the irradiated square edge and (b) corresponding SAD pattern. (c) A image of the silicide film and islands taken at a place 20 μm away from the edge and (d) its SAD pattern.

EDS spectra are shown in Fig. 6 for the silicide island, silicide film, and the surrounding matrix. They are all measured at the area about 15 μm away from the irradiated square edge.

The height of Pd Lα peak for the island (Fig. 6a) is higher than that for silicide film (Fig. 6b). Although the exact concentration of each element can not be estimated by EDS spectra due to the bi-layer film configuration, it reveals that the island contains more Pd than the film, and that this multi phase film consist of two elements, Pd and Si. Analysis of the SAD pattern in Fig. 5b supports the coexistence of PdSi (100) among Pd_2Si. PdSi has an orthorhombic structure with lattice parameter of 0.56, 0.34 and 0.61 nm for the a-, b- and c-axes, respectively.

The island formation is observed in the Pd silicide/ Si system without FIB irradiation after annealing at 673K 15 minutes. The suppression of the island formation and the formation of the new silicide phase are unique phenomena appearing only with the FIB irradiation. It is assumed that the area near the FIB irradiated area has suffered from radiation damage by the beam broadening of the FIB, and that the radiation induced lattice defects and subsequently enhanced diffusion may result in the formation of the new phase. This is considered observable evidence of the FIB beam broadening effect.

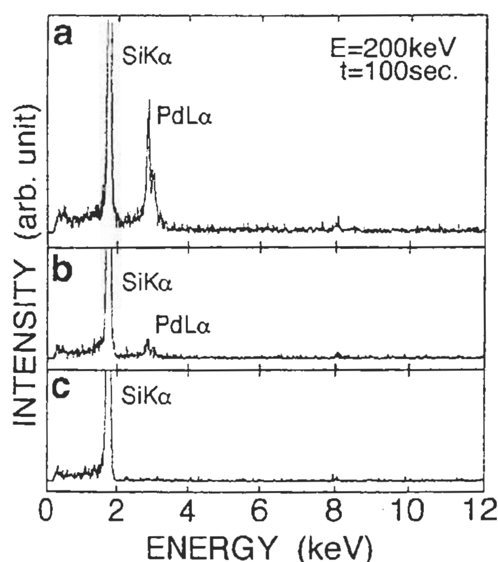

Fig. 6 EDS spectra taken at the place about 15 μm away from the irradiated square edge. (a) A spectrum of Pd island, (b) spectrum of Pd film, and (c) spectrum from the surrounding matrix.

On the bulk substrate, the Pd_2Si phase is reported to be stable up to about 973 K and then transforms to PdSi. The transformation from Pd_2Si to PdSi at much lower temperature induced by ion beam bombardment has been reported by others [11]. They attribute the low temperature reaction to the collision cascades around the primary ion track. In the present case, it is likely that Ga ions from the tail of the FIB profile have worked as the defect generator and contributed to the formation of PdSi at 673 K. Presumably the defects also prevented the Pd silicide film from aggregating to make islands. The relatively small amount of Si in a thin film configuration (TEM sample), which is different from a bulk specimen, may also be one of the factors for the reaction.

Near-noble metals (Ni, Pt and Pd) form a metal rich silicide phase (M_2Si) at the early stage of annealing (at - 473K). Ni and Pt grow a second phase (MSi) at about 573-673K, but the formation of Pd_2Si requires much higher temperature (about 973K) [12]. The reason for this high transformation temperature is considered to be due to the low interface energy of the Pd_2Si / Si system [13], small ΔG_v of the reaction [14] or the thermal stability of Pd_2Si / Si interface [11]. Taking into account the fact that both ion bombardment [11] and the existence of other atoms [15] lower the transformation temperature, the reaction from Pd_2Si to PdSi is likely to be caused by the imperfection of the interface. Since the reaction is nucleation controlled [16], defects, damage, strain, or impurities can break the interface stability and help to produce PdSi nuclei. Obviously our results support this tendency. Injected Ga ions and secondary defects may play the role of nucleation center of PdSi so that the partial transformation of Pd_2Si into PdSi at relatively low temperature has been achieved.

The present results suggest the importance of the beam broadening effect in the lithography field. Even outside the irradiated area, there is a possibility that the radiation damage induces some unexpected reactions. Post irradiation annealing may accelerate this tendency and produce other phases. In the case of the Si-Ni system, precipitation of Ni rich silicide is observed [8,10]. The present data suggest the formation of Si rich silicide in Si-Pd system. Thus it is important to select the appropriate irradiation place so that no extra reaction will happen. These phenomena can only be observed by the FIB/TEM system, not by the conventional evolution methods such as scanning electron microscopy (SEM).

4. Conclusions

FIB irradiation of thin Pd silicide layers on Si TEM films was carried out and studied using an in-situ TEM. Square areas on sides of 4 by 4 μm were patterned at room temperature with a 25keV Ga^+-FIB attached to the TEM. The structural changes after the FIB irradiation showed an uniform milling. Annealing at 673 K for 15 minutes resulted in the formation of Pd silicide islands outside the central FIB irradiated area, but this island formation is suppressed, and the silicide film remained near the irradiated area. Enrichment of Pd in silicide islands was shown by EDS. SAD patterns of the remaining silicide film indicate the partial transformation of the Pd silicide into another Si enriched silicide phase. The beam broadening of the FIB is responsible for the suppression of the island formation and the formation of the other silicide phase.

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