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Diffusion-accompanied Phase Transformation of $TiSi_2$ Film Confined in Sub-micron Area

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Phase transformation of $TiSi_2$ confined in sub-micron area of which the size is around or smaller than the grain size of C49 $TiSi_2$ phase is studied. It has been known that the C49 to C54 phase change is massive transformation that occurs abruptly starting from C54 nuclei located at triple point grain boundaries of C49 phase. When the C49 phase is confined in sub-micron area, however, the massive phase transformation is observed to be hindered due to the lack of the triple point grain boundaries of C49 phase. Heat treatment at higher temperatures starts to decompose the C49 phase, and the resulting decomposed Ti atoms diffuse to, and react with, the underneath Si material to form C54 phase that exhibits spherical interface with silicon. The newly formed C54 grains can also trigger the massive phase transformation to convert the remaining undecomposed C49 grains to C54 grains by serving as nuclei like conventional C54 nuclei located at triple point grain boundaries.

Key words: Phase transformation, Silicide, Grain boundary, Post annealing

I. Introduction

Titanium disilicide ($TiSi_2$) has been widely employed by the semiconductor industry for the self aligned silicide (SALICIDE) process in metal-oxide-semiconductor field-effect transistors (MOSFET), due to its high electrical conductivity and good thermal stability.[1)] Upon heating a titanium metal film deposited on silicon (salicide process), high-resistivity C49 $TiSi_2$ film forms initially, and is converted into low-resistivity C54 $TiSi_2$ phase during the subsequent heating. The phase transformation from C49 to C54, which occurs during the second rapid thermal processing (RTP) in the well-established two-step RTP, therefore, is essential for obtaining low-resistivity $TiSi_2$ film. The phase transformation is believed to occur massively starting at the triple point grain boundaries of C49 phase where C54 phase is nucleated.[2)] When the C49 phase is confined in sub-micron area of which the size is around or smaller than its grain size, therefore, the massive phase transformation is retarded due to the lack of the triple point grain boundaries of C49 phase.[3)]

In this study, we report the first observation of diffusion-accompanied phase transformation of $TiSi_2$ confined in sub-micron size by employing Transmission Electron Microscopy (TEM). When the C49 $TiSi_2$ film is annealed at high temperatures, instead of being transformed to C54 phase, the C49 phase is decomposed into Ti and Si atoms first. The produced Ti metal atoms diffuse to, and react with, the underneath silicon to form the C54 phase that is stable at the high annealing temperatures.

II. Experiment

The used (001) silicon wafers are p-type 4 degree off to (100) direction with electrical resistivity of 9-12 ohm·cm. Two types of samples are fabricated to study the phase transformation of $TiSi_2$ confined in a small area; line type and disk type. The fabrication procedure for the line type sample is same as that for typical MOSFET gate, while that for the disk type sample is same as that for typical metal contact to silicon substrate. Fig. 1 shows a schematic fabrication flow of the gate and the resulting schematic view. Gates are prepared by depositing a fine-grained polycrystalline silicon of 250 nm in thickness over 4.5 nm thick silicon dioxide that is thermally grown on a bare silicon wafer. After line patterning, a CVD SiO_2 film of 200 nm in thickness is deposited to form a sidewall spacer. Following the formation of the sidewall spacer, a portion of the wafer surface is amorphized by an arsenic implantation (PAI: pre-amorphization implantation) at 15 KeV with the dose of 3×10^{11} cm^{-2}. Ti film of 35 nm in thickness is deposited by DC sputtering at a base pressure of 1×10^{-8} Torr. Silicidation is performed by employing the well-established two-step RTP in an N_2 ambient. The first RTP conditions for conventional and pre-amorphized samples are 715°C and 20 sec, and 680°C and 30 sec, respectively. The second RTP is treated at 800°C for 30 sec for both samples. The samples are post annealed at temperatures ranging from 800°C to 950°C for 30 sec.

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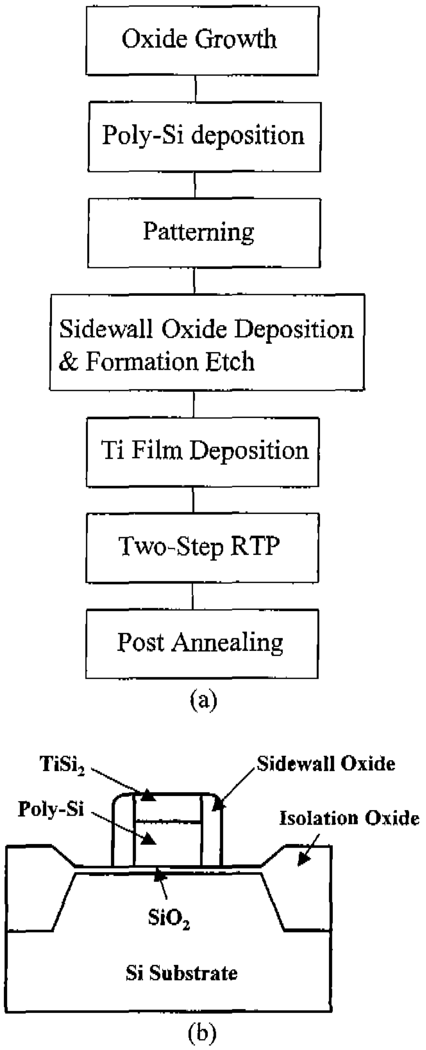


Fig. 1. Schematic fabrication flow of (a) the gate and (b) the resulting view.

Metal contacts are prepared by depositing a CVD SiO_2 film of 1 μm in thickness on a bare silicon wafer. After hole patterning, Ti film of 15 nm in thickness is deposited in the holes by Ion Metal Plasma (IMP) DC sputtering, and followed by the deposition of TiN and W films. The first and second RTPs are conducted at 650°C for 30 sec, and at 850 °C for 30 sec, respectively. Transmission electron microscopy (TEM: Phillips CM200 with field emission gun) is used to analyze $TiSi_2$ phase transformation, and cross-sectional TEM specimens are prepared by focused ion beam (FIB: Micrion 2500). FIB technique is essential in preparing the TEM specimens, due to its unique capability of probing a specific area for thinning. Especially gate specimens are fabricated along the gate lines, so that the viewing area is increased by two orders of magnitude, compared to specimens fabricated across the gate lines.[4]

III. Results and Discussion

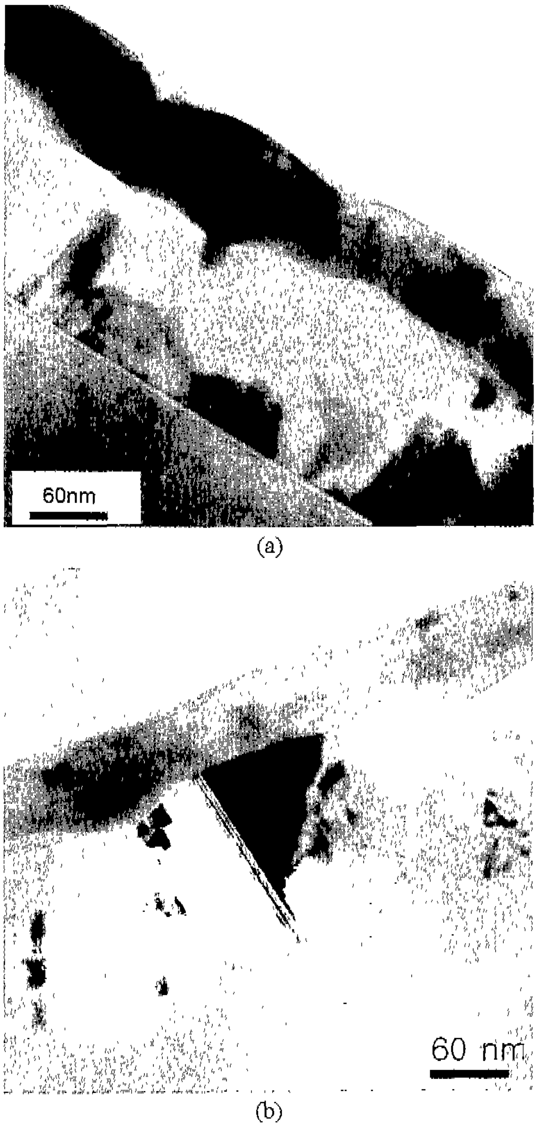
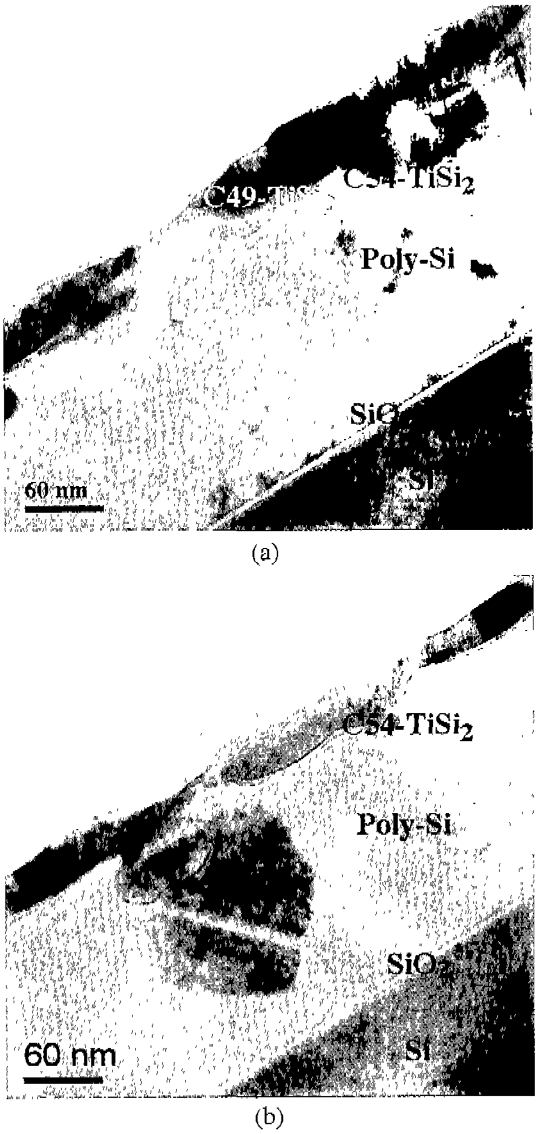


Fig. 2. Cross-sectional TEM pictures of $TiSi_2$ film grown on a 0.2 μm polycrystalline silicon gate (a) without and (b) with PAI treatment.

Fig. 2 shows cross-sectional TEM pictures of $TiSi_2$ film grown on 0.2 μm polycrystalline silicon gates (a) without and (b) with PAI treatment exhibiting no morphological difference between the two films. According to the result of four-point probe measurement, however, the PAI treated gates are completely transformed into C54 phase during the two-step RTP, whereas the untreated, conventional gates retain most of the C49 phase.[5] This result is mainly due to the availability of the triple point grain boundaries in the PAI treated sample, where the boundaries serve as heterogeneous nucleation sites of the C54 nuclei.

Fig. 3 shows cross-sectional TEM pictures of conventional $TiSi_2$ without PAI treatment after post annealing at 950°C for 30 sec. Fig. 3-a shows that the untransformed C49 phase is thinned by its decomposition during the post annealing. The newly formed C54 grains are located at the underneath



(a)

(b)

Fig. 3. Cross-sectional TEM pictures of TiSi$_2$ without PAI treatment after post annealing at 950°C for 30 sec, showing (a) thined C49 phase and (b) transformed C54 phase.

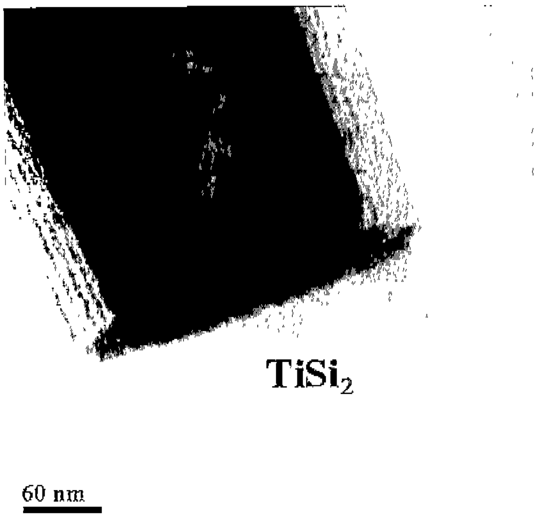


Fig. 4. A cross-sectional TEM picture of TiSi$_2$ film grown on a 0.3 μm contact hole after two-step RTP.

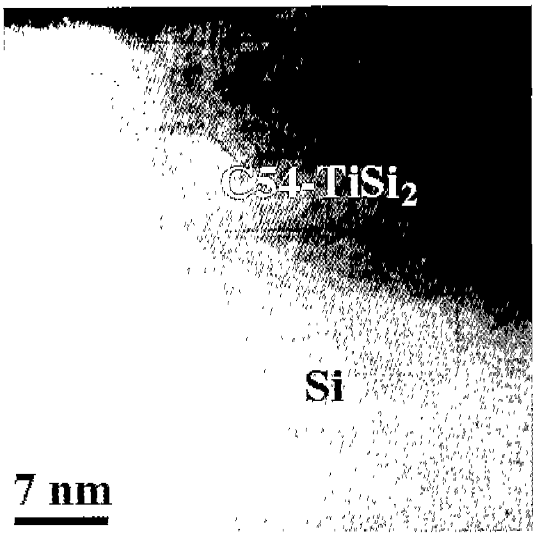


Fig. 5. A cross-sectional HRTEM picture of TiSi$_2$ film grown in a 0.3 μm contact hole after two-step RTP.

polycrystalline silicon in spherical shape. C54 phase was not observed under TEM, when the C49 phase was post annealed at temperatures ranging from 800°C to 900°C with 50°C interval for 30 sec, respectively. The decomposition of C49 grains may generate pure Ti metal atoms and allow them to diffuse to, and react with, the underneath polycrystalline silicon to form C54 grains. The formation of C54 phase instead of C49 phase is favorable, as C54 is the stable phase at this high temperature.1) It should be pointed out that C54 grains show spherical interfaces, while C49 grains show relatively flat interfaces. This feature has been reported in the case of CVD TiSi$_2$ film.6) They observed both the C49 and C54 grains with different interface morphologies, and explained the difference by the fact that the silicon source is from the gas for C49 phase, and from the underneath silicon for C54 phase, respectively. Both phases formed in this study, however, require the silicon source from the underneath silicon, as the phases are formed through the reaction between Ti film and silicon. From the morphology observation of sputter-formed TiSi$_2$ grains as shown in Fig. 3(a), therefore, the interface morphology seems to be mainly determined by crystal structure relationships between TiSi$_2$ and Si, not by the difference of the supply of the silicon source.

Fig. 3(b) shows another region where most grains are transformed to C54 phase. In this case, the newly formed C54 grains are connected to the main TiSi$_2$ film, and induce the C49 to C54 phase transformation. The C49 to C54 phase transformation in this case is, therefore, believed to be initiated from the newly formed C54 grains and to occur massively in nature.

Fig. 4 shows a cross-sectional TEM picture of $TiSi_2$ film grown on a 0.3 μm contact hole after two-step RTPs at 650°C for 30 sec and 850°C for 30 sec. The formed C54 grain in the contact hole shows the same spherical interface with the underneath silicon substrate as those in gate lines do. The observed C54 grains in the contact holes are all located at the central region of the contact hole. This may be explained by the fact that the curved edge region is thermodynamically unfavorable for nucleation of new phases than the flat central region is.[7)]

Fig. 5 shows a cross-sectional HRTEM picture of $TiSi_2$ film grown on a 0.3 μm contact hole. The interface between the C54 grain and Si substrate is atomically rough, indicating incoherent interface. The interface morphology can be explained by considering the crystal structures of C49 and C54 phases. The tetragonal structure of C49 phase can reduce the lattice mismatch with the underneath Si substrate by rotating 45 degrees along the b-axis of the C49 phase, while the orthorhombic structure of C54 phase cannot. Therefore, the interface between C54 and Si becomes incoherent at smaller grain size during the grain growth than that between C49 and Si does. The interface energy term competes with the strain energy term for energy minimization, when the interface between C54 and silicon becomes coherent. However, when the interface becomes incoherent, the strain energy term needs not be considered for energy minimization as the strain energy stored in the $TiSi_2$ phase is relieved. Furthermore, the interface energy can be minimized by reducing the interface area with the formation of spherical shape, as shown in Fig. 3.

IV. Conclusion

The effect of size confinement on the phase transformation of $TiSi_2$ has been studied with line and disk types of $TiSi_2$ film. The formation of C54 phase is initiated by the decomposition of C49 phase in the line type $TiSi_2$ film, due to the lack of triple point grain boundaries. The C54 $TiSi_2$ phase in the line and disk types shows incoherent and spherical interfaces with the underneath materials.

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