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Characterization of tantalum silicide films formed by composite sputtering and rapid thermal annealing

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Abstract Tantalum silicide films are prepared from a composite $TaSi_{2.8}$ target source and subjected to rapid thermal annealing(500-1100℃, 20sec) in Ar ambient. The formation and the properties of tantalum silicides have been investigated by using 4-point probe, x-ray diffraction, scanning electron microscope(SEM), Auger electron spectroscope(AES), and α-step. It has been found that the sample annealed above 700℃ forms a polycrystalline $TaSi_2$ phase, and grains grow in granular form regardless of the kind of substrates. The mechanism of the formation of tantalum silicide is the nucleation and growth by Ta-Si short range reaction. The tantalum silicide film has the relatively low resistivity(70-72.5$\mu\Omega$-cm) and smooth surface roughness.

Ⅰ. Introduction

The continuing evolution toward higher levels of MOS-IC integration has led to the use of finer design rules, thinner gate oxides, shallower junctions, etc.(1-4) These lead to the introduction of polycide structure(5-8), in which silicides are used on top of polycrystalline silicon. Then the use of self-aligned silicide (sailicide) structures become evident(9-12). The latter involves a silicidation of both the source-drain and gate regions simultaneously, reducing not only the interconnection resistance, but also the series resistance of contacts and diffustion regions.

Tantalum silicide is of great interest for ULSI technology owing to its potential usefulness as gate and interconnection materials and low-resistivity contacts on silicon(13-15).

As part of an effort to understand the formation and properties of tantalum silicide, this paper has made and characterized the film of $TaSi_2$; on previous works(16, 17), we investigated the formation and properties of tantalum silicide by annealing Ta metal films deposited on silicon substrated with or without implanted dopants. However, there are many problems to be solved for its device applications, such as dopant out-diffusion and grain morphology, etc..

To overcome these problems, we investigated the formation and properties of silicide formed by new method, sputtered from a single composite $TaSi_{2.8}$ target. This method gained a reputation of being a source of contamination which is detrimental to the film properties. However, composite target method is practical for VLSI metallization.

In this paper, experimental results on some physicl and electrical properties of tantalum silicide films sputtered from a composite target (Ta - Si / Si system) are presented. Furthermore, it was compared with the properties of silicide formed by annealing a Ta films on Si-substrate(Ta-Si/system).

Ⅱ. Experimental procedures

The substrates used were (100) p-type single silicon wafers (5-20Ω-cm) and polycrystalline silcon substrates. For forming a polycrystalline silicon, silicon wafers were oxidized in dry oxygen to form 1000Å of the oxide layer, and polycrystalline silicon films were depostied on theses oxidized wafers by low pressure chemical vapor deposition (LPCVD) process. The thickness of polycrystalline silicon was about 3000Å. All substrates were dipped in diluted hydrofluoric acid for 2 minutes before being installed into the sputtering system.

The tantalum-silicon composite target was manufactured into a disk form by a series of process of cold pressing, vacuum sintering and powder metallurgy. The target had an atomic silicon-to-tantalum ratio of 2.8, as measured by atomic absorption spectroscopy, and a density greater than 85%.

The tantalum silicide films were deposited at room temperature onto the bare single and polycrystalline silicon substrates in a Varian 3290 sputtering system. Films were deposited at D.C. power of 1.5KW for 65 seconds to achieve nominal thickness of 2500Å.

The as-deposited films were annealed to drive silicide formation by rapid thermal annealing (RTA) in halogen lamp annealing system. All samples were loaded, annealed, cooled and removed under a steady argon and nitrogen gas purge flow. The temperature was monitored and controlled by a thermocouple attached to a small reference silicon slice positioned within the anneal chamber. RTA temperatures of 500-1100℃ with intervals of 100 ℃ were used for period of 20 seconds.

The structural property of silicide was investigated with XRD and the sheet resistance was measured by the standard linear four-point probe, while α-step was used to investigate the surface roughness of tantalum silicide. The compositional property was studied with AES, and the bonding state of silicide surface was investigated by using electron spectroscopy for chemical analysis(ESCA). SEM cross section views were used to investigate the growth morphology of tantalum silicide.

Ⅲ. Results and Discussion

1. Crystal Structure

Samples of tantalum silicide films on bare Si were analyzed by X-ray diffraction. Figure 1 presents the X-ray diffraction peaks of tantalum silicide as a function of annealing temperature. The as-deposited sample shows the absence of crystallinity in the film, indicating amorphous sturcture, and the films annealed above 700℃ display diffraction peaks belonging to the hexagonal structure of $TaSi_2$. There was no indication of TaSi or Ta_5Si_3 phases in these patterns, in contrast with another refractory metal silicides(18-19). It was also found that the content of $TaSi_2$ phase was increased with increasing annealing temperature. On the basis of X-ray data, it was concluded that the tantalum silicide underwent a phase change at 700℃, and the amorphous state was completely phase-transformed into $TaSi_2$ above 1000℃

Comparing with the tantalum silicide films formed by annealing a Ta films on Si substrate (16), the formation of silicide film by composite target method occured at lower temperature than the former method(Ta/Si system). Since the tantalum silicide by composite target method was formed by the short range reaction in as-deposited Ta-Si films, in contrast to the Ta/Si system, the activation energy is not necessary to remove the native oxide(10-20 Å) that existed at interface between deposited layer and Si substrate, though the etching process are performed.

This is confirmed by the result of native oxide effect in previous work(17). Thus it is considered that the difference of silcide formation mechanism in both methods give rise to the difference of silicide formation temperature.

Identical results were found for samples de-

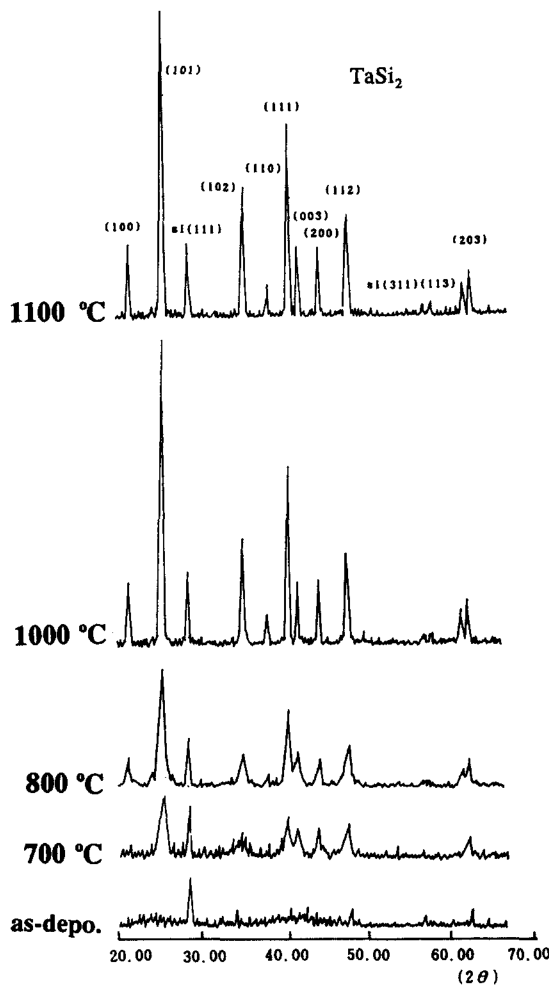


Fig.1 X-ray diffraction peaks of tantalum silicide formed on singlecrystalline silicon substrates

posited on poly-crystalline Si substrate as shown in Figure 2.

2. Sheet Resistance

The sheet resistance of as-deposited films was about 11.5Ω/□ for the sample on single-Si wafer and 9.8Ω/□ for the sample on poly-Si substrate as shown in Figure 3. It was considered that the decrease of sheet resistance with the increase of annealing temperature resulted from the progress of crystallization in silicide layer in connection with XRD results. It was also found that the rapid decrease in sheet resistance was obtained at 700℃, indicating the nucleation of $TaSi_2$ by short range reaction between Ta and Si in deposited layer, and annealing at higher temperature up to 1100℃ changes the sheet resistace only slightly.

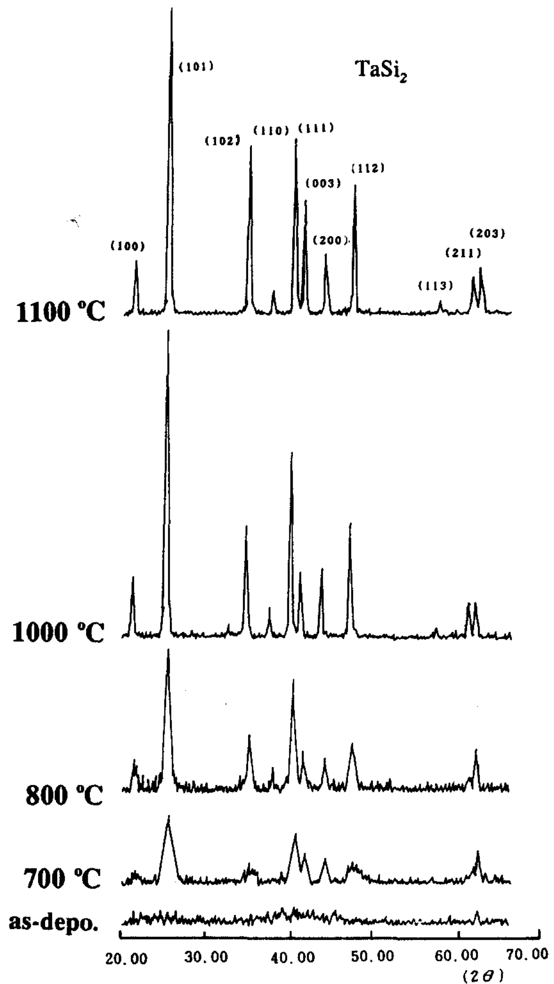


Fig.2 X-ray diffraction peaks of tantalum silicide formed on polycrystalline silicon substrate

Resistivity of silicide layer was calculated with the measured sheet resistance and the thickness of layer. The thickness of the layer was monitored during the sputtering and con-

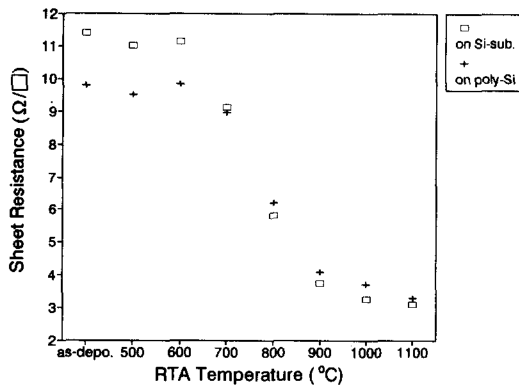


Fig.3 The change of sheet resistance of tantalum silicide formed on single and polycrystalline silicon substrates.

firmed by SEM cross sectional view. From this, the resistivity of silicide obtained at 1000 ℃ and 1100℃ was 70.5-81.7$\mu\Omega$-cm for single Si samples and 66.5-82.7$\mu\Omega$-cm for polycrystailline Si samples. Comparing these values with those given in Ta/Si system(16), it was observed that the sample with composite target method had produced a high resistivity tantalum disilicide phase. This is caused by the impurity inserted during the manufacturing of composite target.

The sheet resistance of tantalum silicide films formed in argon and nitrogen ambient was shown in Table 1. The samples annealed in nitrogen atmosphere had a lower resistance value than that of samples in argon, regardless of the kinds of substrate. It is considered that the grain size of samples in nitrogen is larger than that of argon samples as shown in Figure 4 and figure 5, respectively.

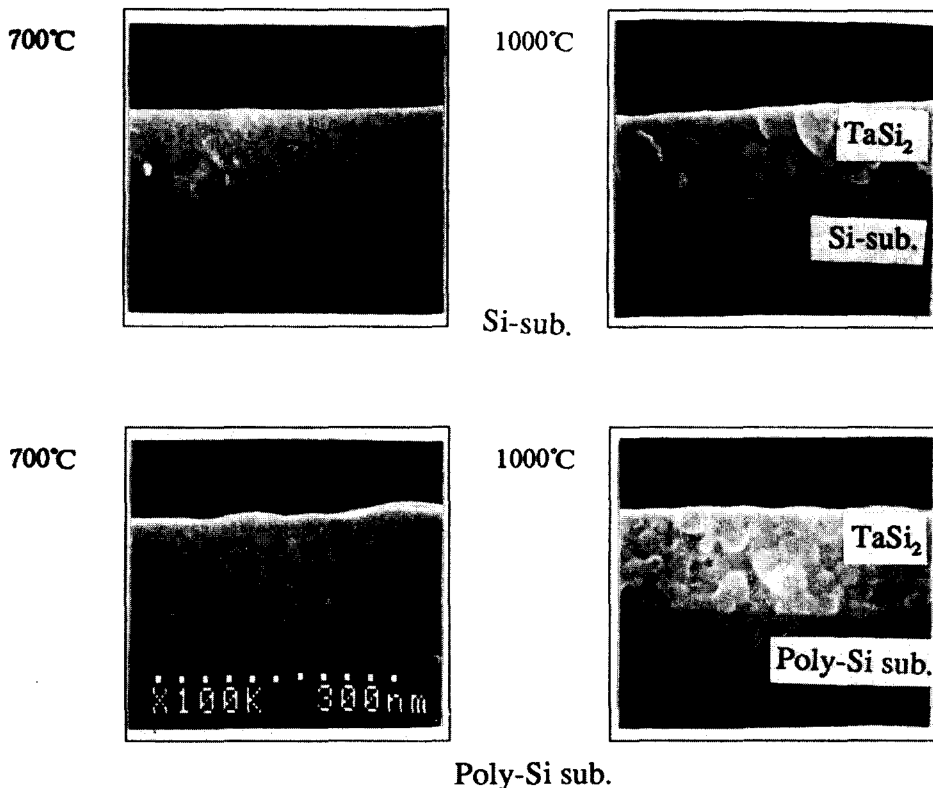


Fig.4 SEM cross sectional views of tantalum silicide formed on single crystalline silicon in nitrogen ambient

3. Morphology

Figure 5(a) and (b) present the SEM cross sectional views of $TaSi_2$ formed on single-Si and poly-Si substrates, respectively. After annealing at 700℃, both samples exhibited the nucleation of $TaSi_2$ from an amorphous state, indicating a reaction between Ta and Si deposited by composite target source, and grain

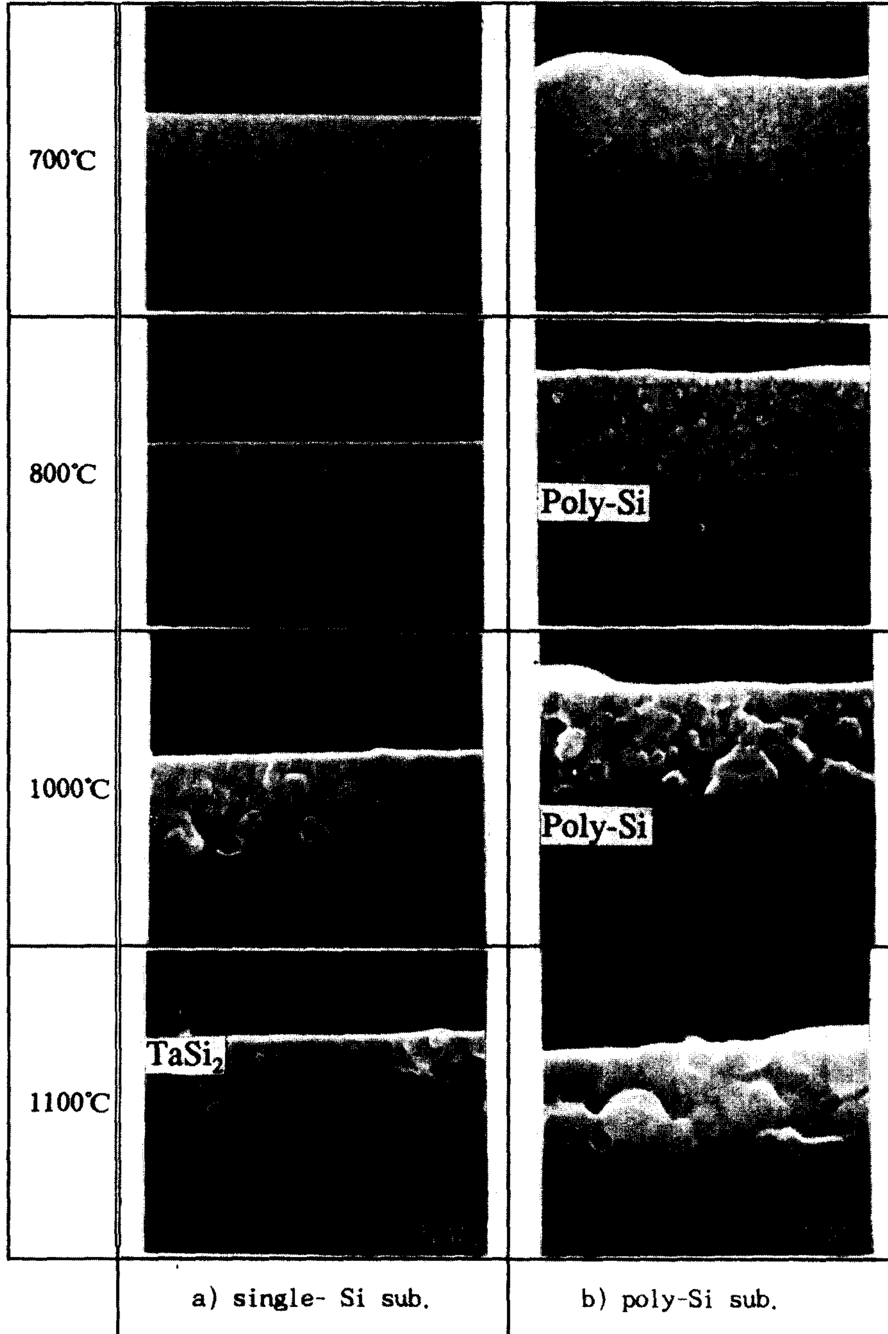


Fig.5 SEM cross sectional views of tantalum silicide formed on (a) single and (b) polycrystalline silicon in argon ambient

Table 1. Sheet resistance valuse of tantalum silicide formed in argon and nitrogen ambient

Unit ; Ohm/square

RTA Temp. \ Atomsphere / substrates		Ar	N_2
700℃	Single-Si	9.1366	7.6976
	Poly-si	8.9618	8.8054
1000℃	Single-Si	3.2660	2.3864
	Poly-Si	3.7072	3.2896

growth with granular structure as the increasing of annealing temperature unlike the columnar structure in the case of Ta/Si system(16). It was considered that the granular structure resulted from the nucleation and growth of $TaSi_2$ by the short range reaction in as-deposited Ta-Si films. It was also found that the $TaSi_2$ formed on poly-Si substrate showed coarser grain than that of singlecrystalline Si substrate, which was caused by the grain boundary in polycrystalline Si enhancing the surface diffusion of Si atoms or Ta atoms.

4. Compositional atomic ratio of silicon to tantalum

A starting material of $TaSi_{2.8}$ was sought for initial evaluation. The as-deposited and annealed films were analyzed by AES for film composition(figure 6). The ratio of silicon to tantalum of as-deposited film was 2.14, and the ratio in samples annealed at 800℃ and 1100℃ was 1.94 and 2.04, respectively. From this figure, it was found that the annealed samples show lower values than 2.14, which was the value for the as-deposited film. During the process of annealing, excess silicon migrated from the silicide layer to the Si-substrate, eventually piling up at the interface between silicide layer and substrate as confirmed in figure 5, indicating the increased thickness of polycrystalline Si.

5. Surface characteristics of $TaSi_2$

In comparing the figure 7 with the earlier results(16), the roughness of the $TaSi_2$/Si interface indicated better adhesion in the case of Ta-Si/Si system than that of Ta/Si system. Figure 7 presents the surface roughness of $TaSi_2$ at various annealing temperatures. This figure clearly shows the smooth surface roughness, having range from 150 to 202±10Å in the case of single-Si substrates, and range from 65 to 164±10Å in the case of polycrystalline Si substrates.

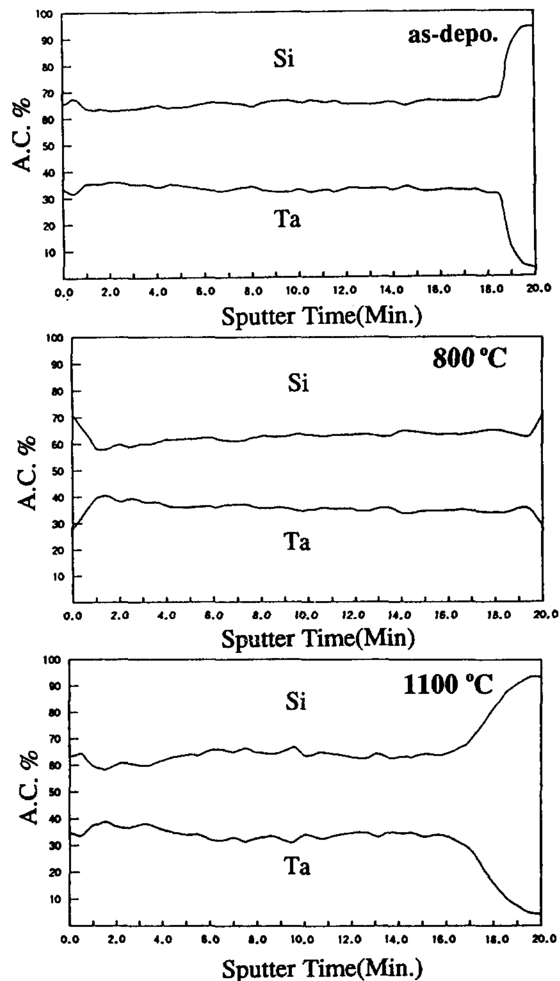
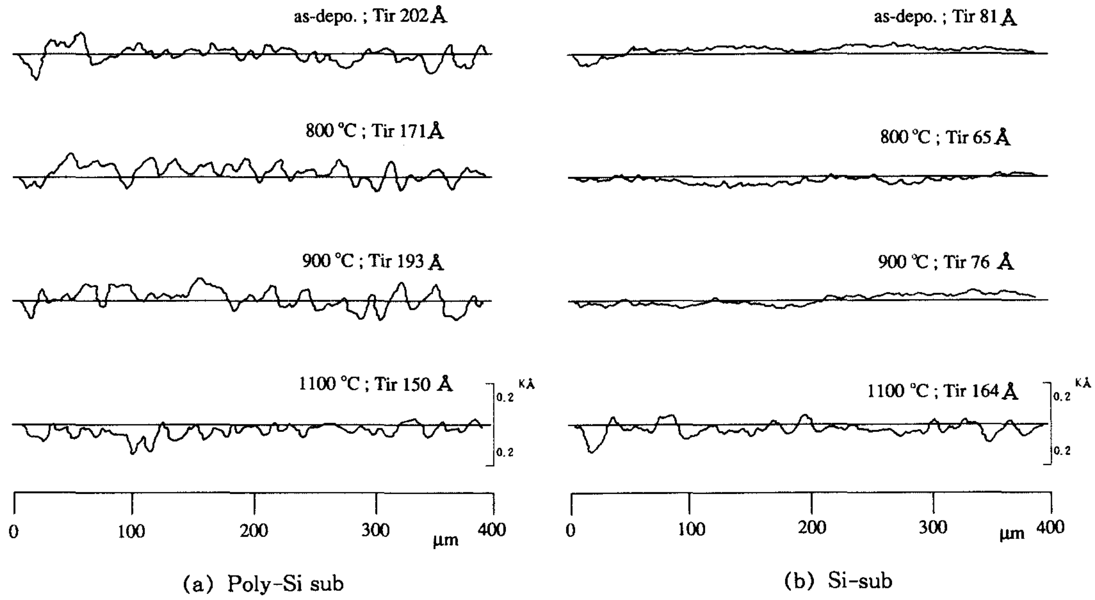


Fig.6 Compositional change of tantalum silicide as a function of annealing temperatures

The surface bonding state of $TaSi_2$ was investigated by using ESCA. The results were presented in figure 8(a) and (b) for the as-de-



(a) Poly-Si sub (b) Si-sub

Fig.7 Surface roughness of tantalum silicide at various annealing temperatures (a) on polycrystailline silicon and (b) on singlecrystalline silicon

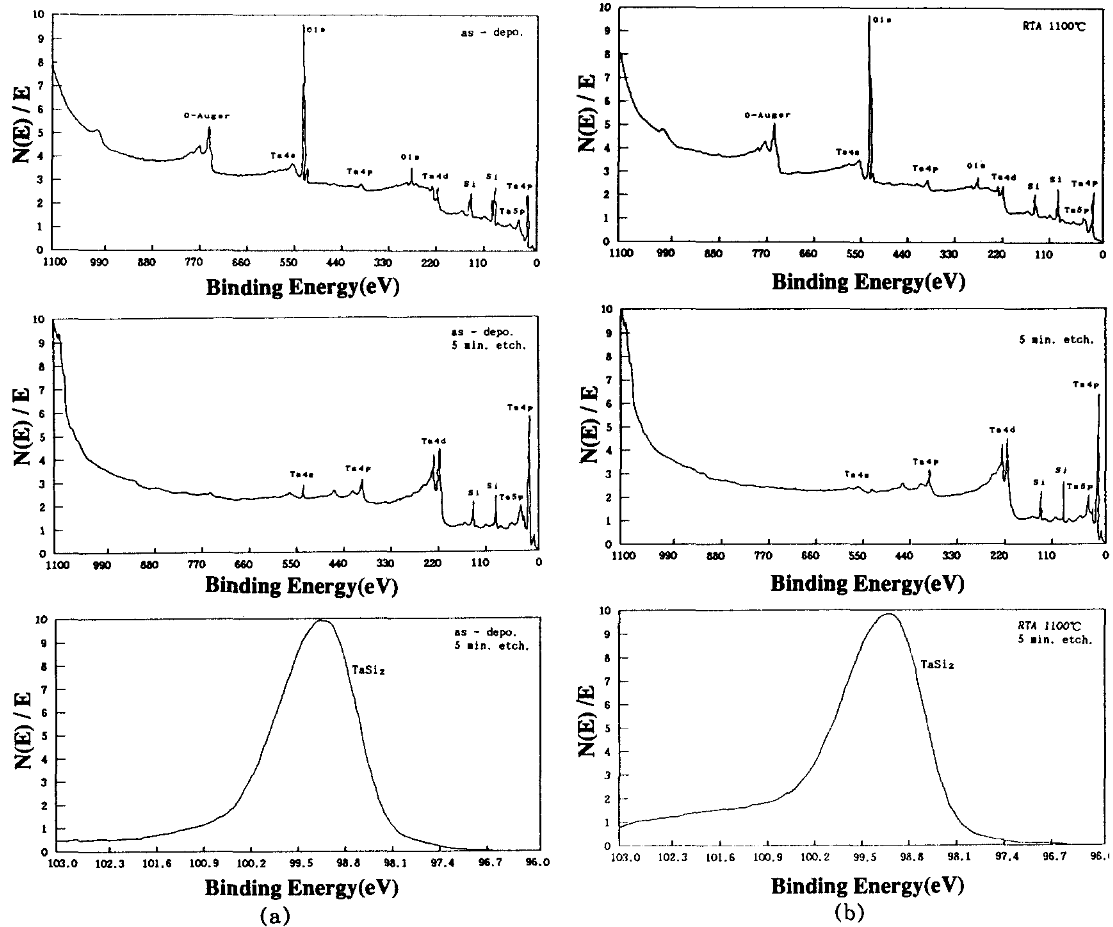


Fig.8 ESCA results obtained from tantalum silicide for (a)as-deposited sample and (b) 1100℃ annealed sample

posited and annealed samples at 1100℃, respectively. In figure 8(a), the oxygen was not detected in etched sample for 5 minutes, but existed at outer surface. It was also found that the as-deposited film was not the mechanical mixture phase of Ta and Si, but the chemically bonded amorphous state. Figure 8(b) shows the similar result with the as-deposited film, because the amorphous state is only transformed into the crystallized phase at higher annealed sample.

Ⅳ. Conclusions

Tantalum silicide films were prepared from a composite $TaSi_{2.8}$ target source and subjected to RTA. The as-deposited films had a silicon-to-tantalum compositional atomic ratio of 2.14.

The sample annealed above 700℃ forms a polycrystalline $TaSi_2$ phase, and grain growth in granular form regardless of the kind of substrates. It was also found that the formation mechanism of $TaSi_2$ was the nucleation and growth by the short range reaction between Ta and Si in deposited layer, and the $TaSi_2$ formed on polycrystalline silcon substrate had a coarse grain in compared with the singlecrystalline silicon substrate. The $TaSi_2$ films has the properties of relatively low resistivity(70-72 $\mu\Omega$-cm) and smooth surface roughness(TIR ; 65-164Å).

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