Phase Evolution by Annealing in V/Al Multilayers Prepared on Thermally Oxidized Si

Naoki Hayashi*, Kenji Morii** and Yutaka Nakayama**

Phase evolution by solid-state reactions in Al/V multilayers ion-plated on thermally grown SiO₂ substrates was investigated by means of X-ray diffraction and transmission electron microscopy, and the possibility for the formation of superconducting phases of V₃Al and V₃Si with the A15 type structure was examined. Annealing at a temperature below about 973 K caused interdiffusion between V and Al layers resulting mainly in a solid-solution of Al in V. After annealing for 1 h at a temperature higher than about 973 K, several compounds were found to form by the reactions between the V-Al solid solution and SiO₂ substrate; A15-V₃Si, unidentified phase which was assumed tentatively as V_xO, and γ -Al₂O₃. The V₃Si phase was nucleated in the amorphous SiO₂ substrate at about 973 K, and grew markedly as the annealing temperature increased up to about 1223 K, but no indications for the formation of the metastable A15-V₃Al phase were detected.

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I. Introduction

It is known that most of the phases having the A15 (Cr₃O-type) structure show superconductivity with a superconducting transition temperature (T_c) as high as about 23 K⁽¹⁾. The A15-V₃Si phase, one of metal-rich silicides, can be successfully produced by thin film reactions between V and SiO₂ overlayered on a Si substrate⁽²⁾⁻⁽⁵⁾. In contrast, the reaction of V on a pure Si layer yielded a totally different phase of one of Si-rich silicides, VSi₂, which is a non-superconducting compound⁽²⁾⁻⁽⁵⁾. The difference in such a phase evolution has been correlated with the effect of oxygen contained in the substrate⁽⁶⁾, but detailed mechanisms or microstructural aspects for the nucleation of the V₃Si on the SiO₂ substrate are still open to discussion.

In the V-Al system, the presence of a meta-stable compound V₃Al with the A15 structure has been pointed out by Holleck *et al.*⁽⁷⁾, though no such phase is found in the equilibrium diagram⁽⁸⁾. The V₃Al phase, if it exists, is anticipated to be a superconductor with high- T_c of about 30 K⁽⁹⁾. Several attempts for synthesizing this phase have been carried out by various techniques: Surikov *et al.*⁽¹⁰⁾ have reported the V₃Al phase formed by long time annealing of a V-25 mol%Al alloy at 1323 K in a quartz ampoule. Hartsough and Hammond have also demonstrated the formation of this phase by co-deposition of V and Al by electron beam heating onto a glass substrate heated at 573 K⁽¹¹⁾. However, attempts based on thin-film reactions for this purpose could barely be available. It is interesting to note that the V₃Al phase could be stabilized by the addition of a small amount of Si⁽¹⁰⁾.

The aim of this work is to investigate the phase evolution in annealed Al/V multilayers which were ion-plated on thermally grown SiO₂. Here, attention is paid to the possibility for the formation of the A15 phases, V₃Si and V₃Al, by solid-state reactions of Al and V under the presence of the SiO₂ layer in the multilayers consisting of rather thick elemental layers (Al $\approx$ 50 nm, V $\approx$ 150 nm).

II. Experimental Procedure

The multilayer was designed to have a structure Al/V/Al/V/SiO₂/Si with two alternating Al and V layers of the thickness of 50 nm and 150 nm, respectively, whose average composition was rather V-rich comparing with the stoichiometry of V₃Al. The excess V was assumed to contribute for the formation of V₃Si. A conventional rf ion-plating method was employed to prepare the Al/V multilayer; high purity Al (99.99%) and V (99.9%) were evaporated sequentially by electron-beam heating, and deposited onto thermally oxidized (001) Si single crystal wafers under a vacuum of better than 2×10^{-2} Pa. Prior to deposition, the oxidation of the wafers was carried out at 1473 K for 2 h in air to grow a SiO₂ layer on the Si substrate; the thickness of the SiO₂ layer was estimated to be of the order of 60 nm⁽¹²⁾. During the deposition of both Al and V, negative bias-potential of DC 200 V was applied to the substrate so as to improve the quality of interfaces of the multilayer. The temperature of the substrate was measured to be as high as about 473 K. The multilayers produced were evaluated by cross-sectional observation with a scanning electron microscope, and were found to be consisting of about 170 nm thick vanadium and about 45 nm aluminum which corresponds to the average composition of about 18 mol% Al.

The multilayered samples were subjected to an isochronal annealing for 1 h under a vacuum of 5×10^{-3} Pa in a temperature range between 473 K and 1273 K.

* Graduate Student, University of Osaka Prefecture.

** College of Engineering, University of Osaka Prefecture, Mozu-memachi, Sakai 591, Japan.

Structural changes caused by the annealing were monitored by measuring sheet resistivity on the Al surface of the samples. The phases formed after annealing were evaluated by the help of X-ray diffraction (XRD) with $\text{CuK}\alpha$ radiation monochromatized by a graphite crystal, and of transmission electron microscopy (TEM) equipped with an energy dispersive X-ray spectrometer (EDS) operating at 200 kV. Thin foils for the TEM observations were prepared from the samples by chemical polishing with a solution of $\text{HF}/\text{HNO}_3 = 1/1$ from the Si substrate of the multilayer.

III. Results

A typical example of the change in sheet resistivity of the annealed samples is given in Fig. 1. The resistivity increased linearly with increasing temperature up to a peak at about 973 K, and followed by a slight decrease at higher temperatures. The result suggests that different type of solid-state reactions was taking place in both sides of the resistivity peak. In the forgoing sections, we show the results on the macroscopic phase evolution evaluated by XRD, and subsequently on the TEM microstructure of the phases observed in the vicinity of the multilayer/ SiO_2 -substrate interface.

1. X-ray diffraction measurements

The XRD patterns of the as-deposited and annealed samples are shown in Fig. 2 for an angular range from 36° to 56° (2θ). The observed diffraction peaks of the as-deposited samples were indexed with the constituting material of the multilayer, Al, V, $\alpha\text{-SiO}_2$ (cristobalite, low) and Si. Here, the peaks of V showed severe line-broadening as well as line-shift to lower angles (Fig. 2(a)). This suggests the presence of fine grained particles and a strong compressive internal-stress in the V layer of the as-

Fig. 1 Change in the sheet resistivity of the Al/V/ SiO_2 /Si multilayered samples annealed at a temperature range between 573 K and 1173 K for 1 h.

deposited multilayer: the latter is considered to be built up mainly during deposition under the negative bias potential, since in the sample deposited without DC bias potential exhibited only small deviation of the diffraction peaks. The TEM observation indicated that the as-deposited sample was composed of polycrystalline Al and V layers with fine grains of the order of about 50 nm.

On annealing the sample up to about 873 K (Fig. 2(b), (c)), the diffraction peaks corresponding to the Al layers disappeared at around 670 K, while the broad peaks from the V layers became sharper and changed their positions in a direction to reduce the lattice parameter as the

Fig. 2 X-ray diffraction patterns for the samples annealed at various temperatures for 1 h; (a) as deposited, (b) 573 K, (c) 873 K, (d) 973 K, (e) 1073 K and (f) 1173 K. The peaks indicated by the symbol ● correspond to the $\text{Al}_{15}\text{V}_3\text{Si}$ phase.

annealing temperature increased, indicating that both the relaxation of the internal stress and the grain growth of the sample were progressed by thermal annealing. Furthermore, the lattice parameter estimated from the peak positions of the 873 K annealed sample ($a=0.3036$ nm) was somewhat larger than that of pure V ($a=0.3023$ nm). If this is assumed due to the diffusion of Al into the V layers, a V–Al solid-solution (A2, bcc) with a concentration of about 15 mol%Al is supposed to be formed⁽¹³⁾, which is close to the mean composition of the present sample (18 mol%Al). Few additional diffraction peaks, which could be indexed by Al_3V , were found after annealing at 773 K, but the phase was unstable and disappeared on further annealing at higher temperatures.

Annealing in the high temperature regime (973–1273 K) altered remarkably the X-ray diffraction pattern (Fig. 2(d)–(f)): The peaks of the V–Al solid solution (A2) retained up to about 1073 K, but disappeared by annealing at high temperatures. At the same time, several additional diffraction peaks were found to appear respectively at about 973 K and 1073 K, and grew steadily as the temperature increased. One group of the peaks formed at 1073 K, indicated by a symbol ● can be satisfactory identified as the $\text{A15-V}_3\text{Si}$ phase, whereas the other group shown by ▼ in Fig. 2 could hardly be attributed to neither of the phases V_5Si_3 , V_2O_5 nor Al_2SiO_5 , which have been reported to be formed by the reaction of V/ SiO_2 bilayer samples^{(2)–(6)}: the peak positions of these phase derived from ASTM cards are compared with that of the 1173 K annealed samples in Fig. 3. As for the unidentified phase, more detailed observations were carried out by TEM, as given below.

The peaks of the SiO_2 substrate were still remained even after annealing at 1173 K (Fig. 3(d)), suggesting that the reactions in the sample were confined among the Al, V and SiO_2 layers. However, no signs for the formation

of the $\text{A15-V}_3\text{Al}$ phase were found in the XRD measurements.

2. TEM observations

The phase formation in the vicinity of the interface between the V–Al solid-solution and SiO_2 substrate was examined by TEM combined with the EDS analysis mainly on the samples annealed at a temperature higher than 973 K.

Typical microstructures observed in the samples annealed at 973 K were shown in Fig. 4(a)–(d). One type of microstructures was characterized by the selected area diffraction (SAD) pattern accompanying with a diffuse halo in addition to several diffraction rings (Fig. 4(a), (b)). The ring pattern was indexed by the $\text{A15-V}_3\text{Si}$ phase as indicated in Table 1, and the halo could be interpreted due to an amorphous SiO_2 , since the radius of the halo corresponds to the line having the maximum intensity of the $\alpha\text{-SiO}_2$. The chemical composition measured by EDS for the phases found in Fig. 4(a) is given in Table 2, which suggests that the corresponding area may be within the SiO_2 side near the $\text{SiO}_2/\text{V-Al}$ interface because of a high concentration of Si. Although the quantitative analysis of oxygen was difficult to perform, fairly large amount of oxygen was detected in this area. Accordingly, fine crystallites of V_3Si were regarded to be formed in the amorphous SiO_2 substrate in Fig. 4(a). Another microstructure, shown in Fig. 4(c), (d), consisted of fine polycrystalline grains (~ 20 nm), and did not accompany halos any more in the SAD pattern. Most of the diffraction rings, however, were hard to index based on several phases such as vanadium silicides (V_5Si_3 , VSi_2), O-rich vanadium oxides (V_2O_5 , $\text{V}_{16}\text{O}_{13}$) or aluminum oxides (Al_2O_3), as in the case of the XRD analysis noted above. The EDS analysis given in Table 2 indicates that the chemical composition of the phase ob-

Fig. 3 Comparison of the diffraction pattern for the sample annealed at 1173 K (f) with the peak positions given in ASTM cards for the several phases; (a) V_5Si_3 , (b) V_2O_5 , (c) Al_2SiO_5 , (d) $\alpha\text{-SiO}_2$ and (e) V_3Si . The peaks marked by the symbol ▼ were hard to index by these phases.

Fig. 4 Transmission electron micrographs and corresponding SAD patterns for the sample annealed at 973 K for 1 h; (a), (b): V_3Si , (c), (d): unidentified, see also Table 1.

served here is V-rich, suggesting the phase being formed in the V-Al side near the interface. In addition, the Al content in the V-Al side is rather low comparing with

Table 1 Comparison of d -spacings (nm) of the phases observed in the samples annealed at 973 K.

(V_3Si)		(b) ⁽¹⁾	X-ray ⁽²⁾	(d) ⁽¹⁾	(hex) ⁽³⁾	
d_{ASTM}	(hkl)	d_{obs}	d_{obs}	d_{obs}	d	(hkl)
0.334	110		0.3352			
			0.2468	0.2465	0.2464	010
0.2364	200	0.2367	0.2358			
			0.2268	0.2275	0.2268	002
			0.2167	0.2151	0.2165	011
0.2112	210	0.2113	0.2102			
0.1928	211	0.1924	0.1923			
				0.1662	0.1668	0.12
0.1668	220	0.1656				
0.1493	310	0.1495				
				0.1419	0.1422	110
0.1364	222	0.1372				
0.1310	320	0.1319	0.1308			
				0.1285	0.1288	013
0.1262	321	0.1267	0.1259			
			0.1231		0.1232	020
			0.1212	0.1220	0.1205	112
0.1181	400	0.1178		0.1183	0.1189	0.21

- (1) corresponding to the results of Fig. 4(b) and (d).
 (2) corresponding to the XRD pattern for the 1173 K annealed sample.
 (3) based on a hypothetical hexagonal lattice with $a=0.2845$ nm and $c=0.4535$ nm.

that in the SiO_2 side (Table 2): parts of the Al atoms in the V-Al were incorporated into the SiO_2 layer.

In order to get crystallographic information of the unidentified phase, micro-diffraction experiments were carried out on a number of relatively large grains. Most of the spot patterns observed could be indexed by a hexagonal lattice with the parameters of $a=0.283$ nm and $c=0.454$ nm, though the crystal structure was not determined. The angular positions of the diffraction rings in Fig. 4(d) were also indexed by using these parameters (Table 1). Typical micro-diffraction patterns with low indices are shown in Fig. 5.

In addition to the phases described above, two other types of microstructures could be remarked in the sample annealed at a temperature higher than about 1073 K at which the phase evolution seemed to be almost completed. Figure 6(a)–(c) shows the phases found in the vicinity of the SiO_2 substrate. One is composed of well-developed coarse grains accompanying with sharp spot

Table 2 EDS analysis for the phases formed after annealing at 973 K.

Phase	Composition (mol%)			
	V	Si	Al	O ⁽²⁾
(a) ⁽¹⁾	12.4	82.1	5.7	—
(c) ⁽¹⁾	92.1	6.4	1.5	—

- (1) corresponding to Fig. 4(a) and (c), respectively.
 (2) qualitative analysis confirmed the presence of some amounts of O.

Fig. 5 Typical example of micro-diffraction patterns with low indices for the phase found in Fig. 4(c). The spot patterns could be indexed by a hexagonal lattice with $a=0.2845$ nm and $c=0.4535$ nm; (a) [100] and (b) [001] zone, see also Table 1.

patterns in their SAD (Fig. 6(b)), and the other consisted of fine polycrystalline aggregates with rather diffuse diffraction rings (Fig. 6(c)). As indicated in Table 3, the former was identified by the α -SiO₂ phase⁽¹⁴⁾ corresponding to the substrate material, and the latter was attributable to the γ -Al₂O₃ phase with the spinel type structure⁽¹⁵⁾. The formation of the V₃Al phase was also failed to observe by TEM.

Table 3 Comparison of d -spacings (nm) of the phases observed in the sample annealed at 1073 K.

(b) ⁽¹⁾ d_{obs}	(γ -Al ₂ O ₃) d_{ASTM}	(c) ⁽¹⁾ d_{obs}	(α -SiO ₂) d_{ASTM}
0.4559	0.456	0.4062	0.405
0.2786	0.280	0.3485	0.352
0.2407	0.239	0.3152	0.314
0.2279	0.228	0.2480	0.2485
0.1979	0.1977	0.1568	0.1571
0.1525	0.1520	0.1380	0.1379
0.1393	0.1393		

(1) corresponding to the results of Fig. 6(b) and (c), respectively.

Fig. 6 Transmission electron micrograph (a) and corresponding SAD patterns for the sample annealed at 1223 K for 1 h; SAD patterns (b): α -SiO₂ and (c): γ -Al₂O₃ were taken respectively from areas B and C in (a), see also Table 2.

IV. Discussion

The results shown above indicate that the phase evolution of the Al/V/SiO₂ multilayer samples was characterized by the annealing temperature:

Below about 973 K, the interdiffusion between V and Al layers seemed to be a dominant process. The diffusion process progressed to form the V–Al solid solution (A2) in a macroscopic sense, though the Al₃V phase appeared locally in the V/Al interface, which is usually found as the first phase formed by solid state reactions of a V/Al multilayer⁽¹⁶⁾. The Al₃V phase disappeared on annealing at higher temperatures, because of the presence of excess V in the present sample. Although the Al₁₅–V₃Al phase was expected to be formed by reactions between V and Al layers, no such indications were obtained in the XRD and TEM observations. It is usually believed that the formation of a metastable phase in a thin overlayered film was concerned with a high diffusion rate of constituting atoms, which could be provided by a high density of grain boundaries or of lattice defects induced during the deposition of films, and by the thickness of the elemental layers with a submicron order⁽¹⁷⁾. Since the present multilayered samples were produced by rf ion-plating under the bias potential, fine grained V and Al layers with fairly high internal stress were obtained (Fig. 2). Accordingly, the microstructure of the present sample could lend itself to the increase in diffusivity. However, the thickness of the elemental layers of the present multilayered sample is thought to be rather thick (V: 170 nm, Al: 45 nm), and therefore the effective diffusion rate in the sample may not be enhanced high enough for the formation of metastable phases.

In contrast to low temperature annealing, by annealing at a temperature higher than about 973 K, the V–Al solid solution was diminished, and additional reactions responsible for the nucleation of new phases occurred between the V–Al solid solution and SiO₂ substrate. Consequently, the V₃Si and unidentified phases as well as γ -Al₂O₃ were formed (Figs. 2, 4 and 6).

Oya *et al.*⁽¹⁸⁾⁽¹⁹⁾ have shown by the analysis of ESCA on the reaction of a V/SiO₂ bilayer that oxygen atoms bound to the SiO₂ were incorporated into the V layer, and the interdiffusion between V and released Si occurred. The O atoms can dissolve interstitially in vanadium (A2, bcc), but tend to rearrange into a superlattice at higher oxygen contents beyond about 10 mol%O⁽²⁰⁾. According to the V–O equilibrium diagram⁽²⁰⁾, the β (body centered tetragonal), γ and δ (B1, NaCl type) phases appear in the concentration ranges of 10–22 mol%O, 30–35 mol%O and 45–55 mol%O, respectively. Here, the γ phase is assumed to have a hexagonal lattice, but its crystal structure is uncertain.

Based on this view, in the V–Al side of the V–Al/SiO₂ interface of the sample, the formation of a V–O solid solution or vanadium oxides is expected to occur due to the enrichment of O atoms being diffused from the SiO₂. The unidentified phase observed by the XRD and TEM

(Figs. 2, 3 and 4) may be assumed as a product of such reactions. Taking into account the results that the phase was supposed to have a hexagonal lattice (Fig. 5, Table 1) and was estimated to contain some amounts of oxygen (Table 2), the γ -V_xO ($x \approx 2$) may be one of the candidates for the unidentified phase observed.

On the other hand, in the SiO₂ side close to the V–Al/SiO₂ interface, the concentration of V as well Si tended to increase due to the mutual diffusion of V and O. This may lead to a possibility for the formation of vanadium silicides. The TEM observation showed the V₃Si phase in the amorphous SiO₂ (Fig. 4(a), (b)): the amorphous phase was considered to be formed as a result of the thermal oxidation of the Si wafer, though crystalline SiO₂ was also formed, as found by the XRD measurements (Fig. 3). It is interesting to note the results⁽²¹⁾⁽²²⁾ that the Al₁₅ phases were easy to nucleate and grow out of the amorphous structure. It could be expected, therefore, that if the concentration of V is increased to an appropriate amount for the phase evolution, the V₃Si phase could nucleate in the O-poor amorphous areas in the thermally grown SiO₂ substrate: detailed mechanisms for the nucleation of V₃Si in the amorphous phase are still unclear.

With increasing annealing temperature up to about 1173 K, both the vanadium silicide (V₃Si) and unidentified phase grew markedly and constituted two main phases of the annealed sample (Fig. 2(f)). In addition, other reactions can also be expected to occur locally near the V–Al/SiO₂ interface, especially in the crystalline areas of the SiO₂ substrate. The γ -Al₂O₃ phase observed on the crystalline SiO₂ substrate (Fig. 6) is regarded as a product of the reaction between Al diffused from the V–Al solid solution and O in the SiO₂ layer.

V. Summary

The phase evolution by solid-state reactions in the Al/V multilayered samples prepared on the thermally grown SiO₂ was investigated by XRD and TEM observations. The results showed that in succession to the development of a V–Al solid solution (A2) due to interdiffusion of V and Al at a temperature below about 973 K, the Al₁₅–V₃Si was nucleated in the amorphous SiO₂ substrate at about 973 K and grew steadily at higher temperatures. The aluminum atoms lend themselves to the formation of γ -Al₂O₃: no indications of the Al₁₅–V₃Al phase were found in the annealed multilayered samples with rather thick constituting layers, Al(45)/V(170)/SiO₂(60).

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