Silane silicidation of Mo thin films

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Silicidation of molybdenum thin films has been obtained for the first time from the reaction of molybdenum with silane (SiH_4). Auger electron spectroscopy measurements indicate a uniform $MoSi_2$ film has been grown. X-ray diffraction data show that films silicidized at relatively high flow rates have a dominant Mo component along with a significant hexagonal $MoSi_2$ phase. Post-reaction annealing in H_2 results in the complete disappearance of Mo with the concurrent increase of various silicide phases ($MoSi_2$, Mo_5Si_3, Mo_3Si). The growth kinetics were investigated as a function of reaction time and temperature and reactant flow rate. The sheet resistance of the reacted films can be controllably varied between that of Mo and of $MoSi_2$. Post-silicidation annealing behavior was found to be strongly ambient dependent. Oxidation of the reacted films resulted in a uniform SiO_2 overlayer.

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INTRODUCTION

Refractory metal silicides are under active investigation as highly conductive interconnect materials for very-large-scale-integrated (VLSI) circuits. Metal silicide thin films have been obtained to data mainly by the following methods: sputtering from the stoichiometric compounds,[1,2] coevaporation of the metal and silicon,[3] and sequential deposition of the individual components followed by sintering.[4] In this paper we report on the silicidation of molybdenum thin films. The reaction of SiH_4 gas with Mo films results in the growth of a continuous $MoSi_2$ overlayer. By this technique it is hoped that one can obtain a self-aligned metal-oxide-semiconductor (MOS) electrode, the so-called "heart-of-Moly", which has both the high conductivity of the metal and the oxidation resistance of the silicide.

EXPERIMENTAL

The experiments performed used oxidized Si substrates. Initially Mo films of 2800 Å were dc Magnetron sputtered using an MRC 603 system. To insure good adhesion, the substrates were preheated for 5 min at 300 °C. A modified Applied Materials AMD 800 Epitaxial Reactor was used for the silicidation process. To prevent oxide growth during the process the system was prepurged with H_2 at room temperature. The reactor temperature was then raised to 1000 °C under cointinuous H_2 flow to provide *in situ* cleaning of the Mo film surface. Following this step, the temperature was lowered to the reaction temperature in the 600–850 °C range. The reactant mixture used was a 10/90 SiH_4/H_2 calibrated source. The main carrier gas was hydrogen and its flow rate was maintained at 30 l/min throughout.

RESULTS

Auger electron spectroscopy (AES) was used to obtain compositional depth profile of the silicidized Mo film. Figure 1 shows the AES profile of a film reacted for 120 sec at 800 °C under a silane flow rate of ~144 cc/min and subsequently oxidized. The profile shows that a uniform molybdenum silicide layer has been obtained. The top SiO_2 layer grown out of the silicide is also quite uniform and the SiO_2-silicide interface appears abrupt.

X-ray diffraction measurements were done with a Siemens D 500 Automated Power Diffractometer to investigate the structure of the reacted films. Three samples were

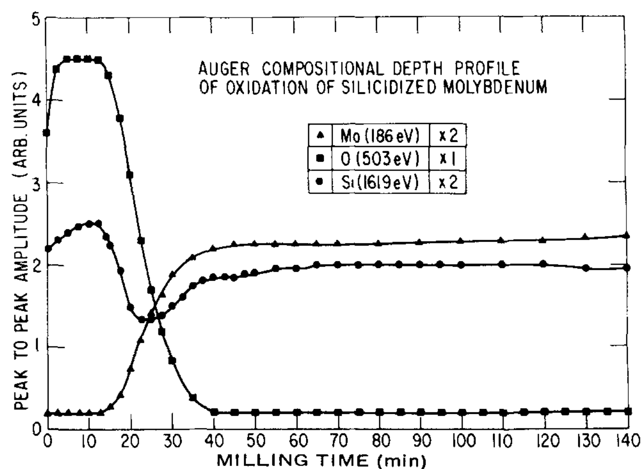

FIG. 1. Auger composition-depth profile of a silicidized molybdenum film which was subsequently oxidized.

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TABLE I. Examination of diffraction peaks obtained from 2800-Å-thick Mo film which was silicidized with 10% SiH_4 (143.5 cc/min) at 800 °C for 60 sec (sample B).

Experimental d (Å)	I/I_m	Mo[a] d (Å)	Mo[a] I/I_m	Mo[a] hkl	h-$MoSi_2$[b] d (Å)	h-$MoSi_2$[b] I/I_m	h-$MoSi_2$[b] hkl	t-$MoSi_2$[c] d (Å)	t-$MoSi_2$[c] I/I_m	t-$MoSi_2$[c] hkl	Others
3.976	40				3.98	10	100				
								3.92	45	002	
3.399	117				3.37	50	101				
3.102	12										Si(111)[d]
2.966	7							2.96	95	101	
2.527	42				2.53	25	102				
2.448	6										Mo_5Si_3(002)[e]
					2.359	16	110				
2.296	28							2.26	70	110	
2.220	1000	2.225	100	110							
2.167	337				2.169	100	111				
2.026	6							2.02	100	103	
1.989	26				1.992	16	200				
								1.96	40	{004, 112}	
1.912	5										Si(220)[d]
1.881	84				1.882	40	112				
								1.60	30	220	
1.582	6				1.584	6	113				
		1.574	21	200							
1.513	9				1.511	6	104				
								1.48	20	{114, 202}	
1.467	14				1.468	20	203	1.41	25	{105, 211}	
1.367	9				1.369	10	212				
1.331	13				1.331	16	114				
								1.308	16	006	
1.300	11				1.298	16	301				
1.284	8	1.285	39	211							
								1.257	45	213	
1.241	6							1.241	10	204	
1.229	8				1.229	10	302				
1.148	8				1.147	10	220				
1.133	8				1.138	10	115	1.132	30	{116, 220}	
		1.1127	11	220							
1.109	38				1.107	4	214				Si(422)[d]
1.089	7				1.090	6	006	1.088	8	222	
1.057	4							1.057	12	{301, 107, 215}	
1.043	6				1.046	4	312				Si(511)[d]
1.028	6				1.030	6	304				
1.015	22				1.017	20	223				
								1.012	25	206	
		0.9952	17	310							
0.985	3				0.988	2	215				
0.910	3	0.9085	7	222							

[a]Standard powder diffraction pattern 4-0809.
[b]Standard powder diffraction pattern 17-917.
[c]Standard powder diffraction pattern 6-0681.
[d]Peaks from silicon substrate, which is 2 to 3° off (111).
[e]Standard powder diffraction pattern 17-415.

studied: (1) a Mo film reacted at a low SiH_4 flow rate, sample A in Fig. 3; (2) a Mo film reacted at a high flow rate, sample B in Fig. 3; (3) a film reacted under the same conditions as sample B and then annealed in H_2 for 45 min at 1000 °C, sample C in Fig. 6. The actual x-ray diffraction data for samples B and C are tabulated in Tables I and II, respectively. The salient features of the x-ray experiments are highlighted in Fig. 2. The film silicidized at low flow rate is composed almost entirely of Mo with only a minute amount of hexagonal $MoSi_2$ (h-$MoSi_2$) present. At a higher reactant flow rate, Sample B, the Mo peak still dominates but a substantial increase in the h-$MoSi_2$ concentration is observed. Annealing the silicidized film, sample C, resulted in a drastic phase change. The Mo peaks are now completely absent and three other molybdenum silicide phases are observed: t-$MoSi_2$, Mo_5Si_3, and Mo_3Si. The formation of these silicides

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TABLE II. Examination of diffraction peaks obtained from 2800-Å-thick Mo film which was silicidized with 10% SiH_4 (143.5 cc/min) at 800 °C for 60 sec and then annealed in H_2 at 1000 °C for 45 min (sample C).

Experimental		t-$MoSi_2$ [a]			Mo_5Si_3 [b]			Mo_3Si [c]			Others
d (Å)	I/I_m	d (Å)	I/I_m	hkl	d (Å)	I/I_m	hkl	d (Å)	I/I_m	hkl	
3.918	459	3.92	45	002							
								3.46	18	110	
3.234	54				3.23	20	211				
3.119	58										Si(111) [d]
3.042	47				3.04	20	310				
2.963	956	2.96	95	101							
2.451	847				2.443	10	002	2.45	17	200	
					2.406	10	400				
2.345	23				2.342	60	112				
2.307	120										? [e]
2.264	562	2.26	70	110							
2.185	176				2.174	20	202	2.19	100	210	
2.152	23				2.149	60	420				
2.107	49				2.102	50	411				
2.025	1000	2.02	100	103				2.00	45	211	
1.990	69				1.986	100	222				
1.961	28	1.96	40	004, 112							
1.602	15	1.60	30	220				1.74	4	220	
								1.55	5	310	
1.527	18				1.522	10	620				
1.480	118	1.48	20	114, 202	1.491	10	512				
					1.437	2	541				
1.409	99	1.41	25	105, 211					1.41	18	222
1.385	19				1.395	10	323				
					1.376	10	631				
					1.363	10	532				
								1.36	32	320	
1.339	24				1.339	20	602, 413				
1.304	24	1.308	16	006				1.31	21	321	
1.254	225	1.257	45	213							
1.238	20	1.241	10	204							
1.225	101							1.22	17	400	
					1.169	10	642				
								1.15	2	411, 330	
1.130	141	1.132	30	116, 220							
1.086	26	1.088	8	222							
1.066	29			301							
1.058	67	1.057	12	107, 215								? [e]
1.055	51										? [e]
1.043	24										? [e]
1.013	92	1.012	25	206							

[a]Standard powder diffraction pattern 6-0681.
[b]Standard powder diffraction pattern 17-415.
[c]Standard powder diffraction pattern 4-0814.
[d]Peak from silicon substrate, which is 2 to 3° off (111).
[e]Not identified.

is the result of the reaction of the h-$MoSi_2$ and Mo. Similar results have been reported[5] in the reaction of silicide-coated bulk Mo.

The growth kinetics were investigated as a function of reaction time and temperature and reactant flow rate. In Fig. 3, the sheet resistance of films reacted at 800 °C is plotted as a function of reaction time for two SiH_4 flow rates. Prior to any reaction, the sheet resistance measured was 0.33 $\Omega/\square$ indicating a resistivity of $\sim 10\,\mu\Omega$ cm. At the lower flow rate a slight increase in R_s was observed for a reaction time up to 2 min. This is consistent with the x-ray data which indicated the formation of only a minute amount of $MoSi_2$ under these conditions. However, at the higher flow rate of ~ 144 cc/min the sheet resistance increased more rapidly, effectively tripling after ~ 100 sec. An even more rapid increase was observed beyond 100 sec reaction time. For 120 sec, an R_s of $\sim 1.6\,\Omega/\square$ was measured which approaches the sheet resistance of sputtered $MoSi_2$ films of a thickness approximately equal to that of the initial Mo film. The flow rate dependence of the reaction was investigated over a SiH_4 flow rate range up to 250 cc/min. As shown in Fig. 4, the R_s of the reacted films inreased linearly with flow rate over this range.

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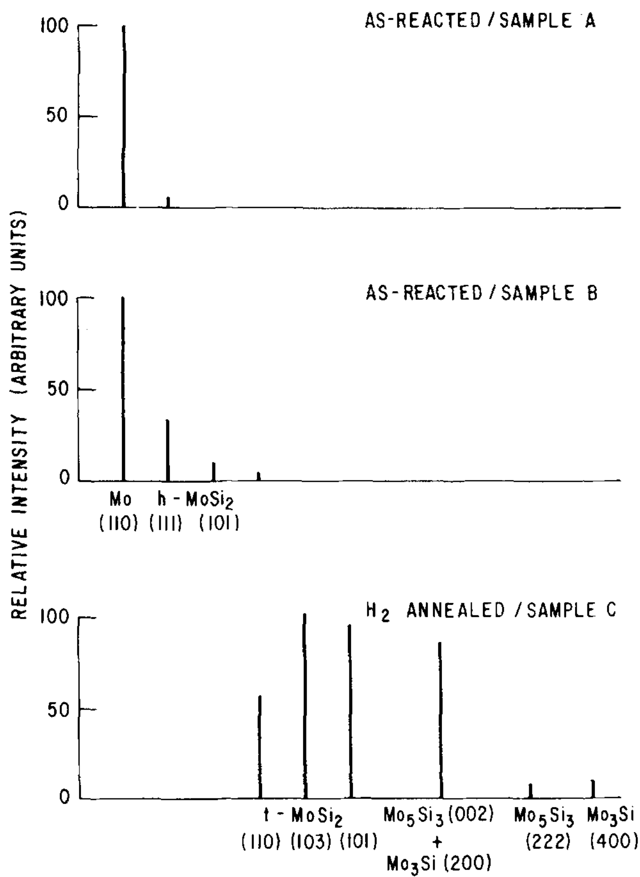

FIG. 2. X-ray diffraction peaks of as-reacted and annealed silicidized Mo films.

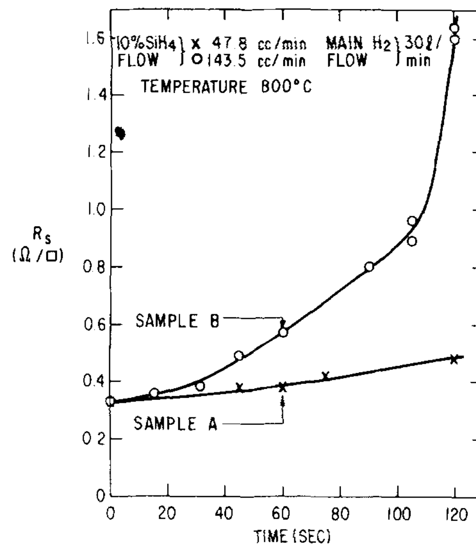

FIG. 3. Sheet resistance of silicidized molybdenum films as a function of reaction time.

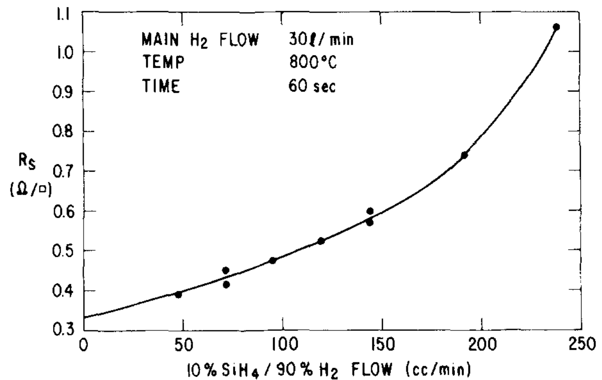

FIG. 4. Sheet resistance of silicidized molybdenum films as a function of silane flow rate.

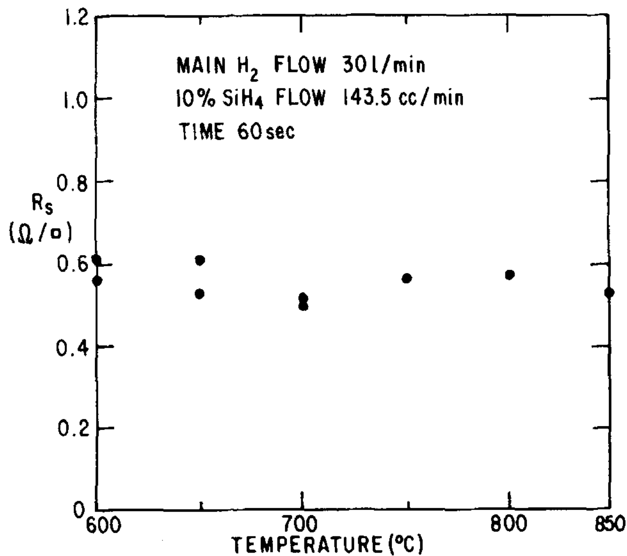

FIG. 5. Sheet resistance of silicidized molybdenum films as a function of reaction temperature.

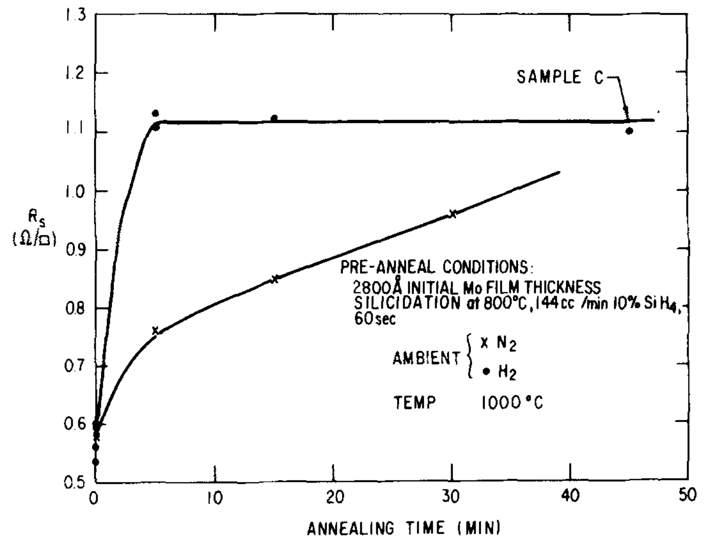

FIG. 6. Sheet resistance of annealed silicidized molybdenum films as a function of anneal time.

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This indicates that $MoSi_2$ growth in this range is mass transfer rate limited. This was also confirmed by the "loading" effect observed when films on multiple substrates were simultaneously reacted.

The dependence of the sheet resistance on reaction temperature is illustrated in Fig. 5. In the temperature range investigated, 600–850 °C, only slight variation in R_s was observed for a 60-sec reaction time and a reactant flow rate of ~ 144 cc/min. Under these conditions, the reaction rate is apparently not the determining factor in silicidation process.

The effect of annealing on the sheet resistance of partially silicidized films is shown in Fig. 6. Samples which had been reacted for 60 sec at 800 °C and a 144 cc/min SiH_4 flow rate were annealed in H_2 and N_2 ambients at 1000 °C. In the case of N_2 anneal, the R_s showed a gradual increase in the first 5 min of annealing. Subsequent anneals up to 45 min resulted in no further increase. In the x-ray data shown earlier (for sample C) no Mo is left after the 45-min anneal in H_2. This is consistent with the sheet resistance measurements of $R_s > 1\ \Omega/\square$, which is typical of silicide films.

CONCLUSION

In conclusion, the silicidation of Mo thin films has been shown for the first time. The reaction of SiH_4 with Mo films was shown to be controllable over a wide SiH_4 flow rate range and to result in uniform $MoSi_2$ films.

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