Table 8.
Ta/SiN, Cr/SiN, Ta/SiO$_2$, and Cr/SiO$_2$ failure surface analysis results

Interface	Peel interface surface	C%	O%	N%	Si%	Ta%	Cr%	Cu%
Ta/SiN*	metal							
Ta/SiN*	substrate							
Cr/SiN	metal	24	51	1	6	—	19	—
Cr/SiN	substrate	12	29	28	28	—	3	—
Ta/SiO$_2$	metal	16	62	—	2	19	—	< 1
Ta/SiO$_2$	substrate	8	65	—	24	2	—	< 1
Cr/SiO$_2$	metal	16	48	—	5	—	31	—
Cr/SiO$_2$	substrate	9	64	—	23	—	4	—

*Sample could not be peeled.

Table 9.
Cr/SiN XPS locus of failure analysis results

Peel interface surface	Element	Observed BE (eV)	Literature BE (eV)	Literature assignment	References
Metal	N1s	396.9	396.7	Cr−N	[31]
			397.4–398.0	Si$_3$N$_4$	[31]
	O1s	531.1	530.0–530.8	Cr-oxide	[31]
			531.2	Cr(OH)$_3$	[31]
			532.5	−Si−O−	[31]
	Si2p	99.3	98.9–99.7	Si^0	[31]
			99.4–100.5	silicide	[31]
		102.1	101.4–101.9	Si$_3$N$_4$	[32]
			101.9–103.0	−N−Si−O−	[29, 32]
			102.0–102.7	−Si−O−	[31]
	Cr2p	574.0	573.8–574.7	Cr^0	[31]
		576.7	575.9–576.8	Cr-oxide	[31]
Substrate	N1s	397.8	397.4–398.0	Si$_3$N$_4$	[31]
			397.6–398.4	−N−Si−O−	[32]
	O1s	530.5	530.0–530.8	Cr-oxide	[31]
		532.1	532.5	−Si−O−	[31]
	Si2p	102.1	101.4–101.9	Si$_3$N$_4$	[32]
			101.9–103.0	−N−Si−O−	[32]
			102.0–102.7	−Si−O−	[31]
	Cr2p	577.1	575.9–576.8	Cr-oxide	[31]

XPS data obtained from the failure surfaces are summarized in Table 8 for samples shown in Fig. 5. After peeling, all metal and substrate interface surfaces, except for Ta/SiN, were analyzed. A comparison of data in Table 3 to the LOF data in Table 8 shows that the metal concentration at the substrate peel interface surface is lower by a factor of two as compared to the initial surface concentration (sputtering from the chamber during Ar-sputter clean). From the observation that residual metal is present on the substrate and Si-species are present on the metal peel interface, it is suggested that the locus of failure is either in the insulator or between the interfacial reaction products layer and the insulator

3.2.2. Cr/SiN interface. Data were compiled from the high resolution scans of the elements shown in Table 8 from both sides of the peel locus of failure. The Si2p and Cr2p XPS spectra obtained from the metal interface surface after peeling at the Cr/SiN interface are shown in Fig. 6.

High resolution XPS analyses results for Cr/SiN failure interface surfaces are shown in Table 9. The two Si2p peaks from the peeled Cr interface surface are located at 99.3 eV and at 102.1 eV. The latter may be assigned to SiON and/or SiO_x [32]. The

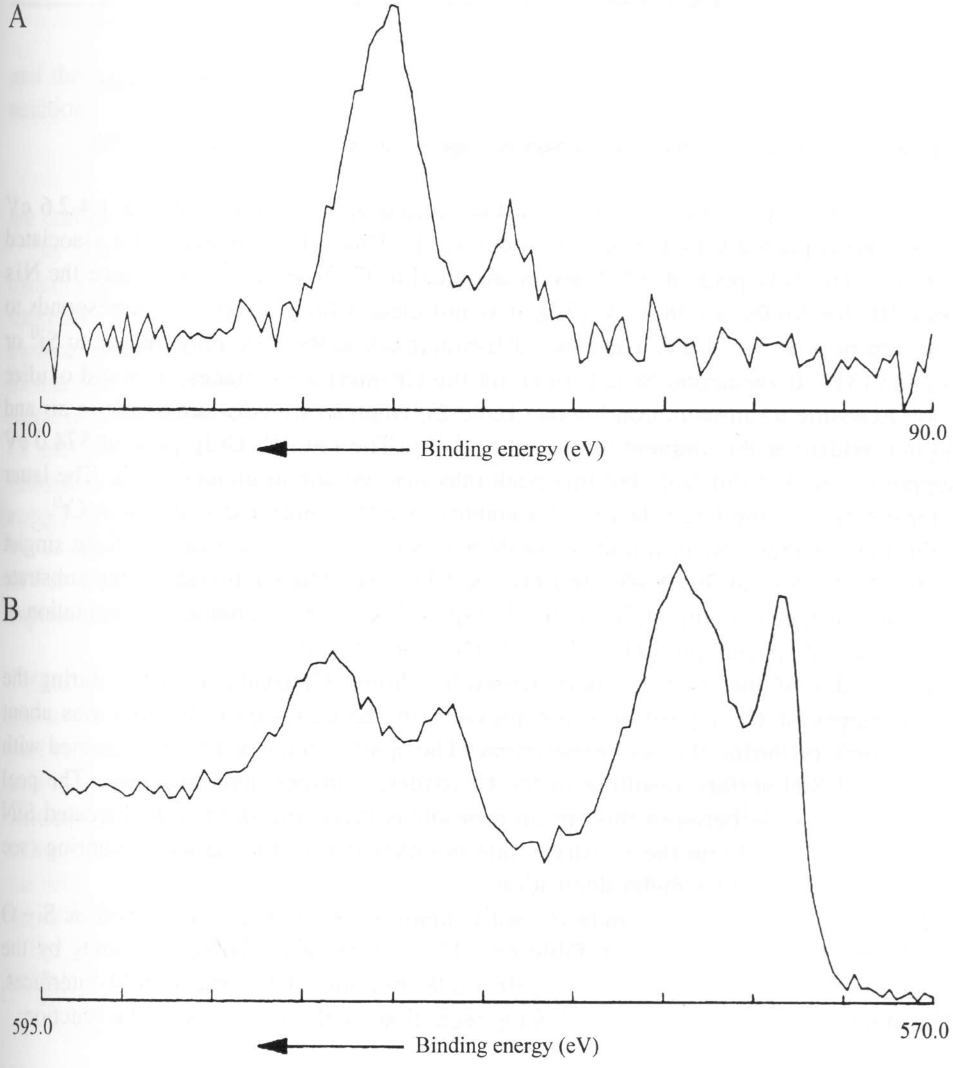

Figure 6. A) Si2p, and B) Cr2p XPS peaks obtained from the peeled Cr interface surface of the Cr/SiN system.

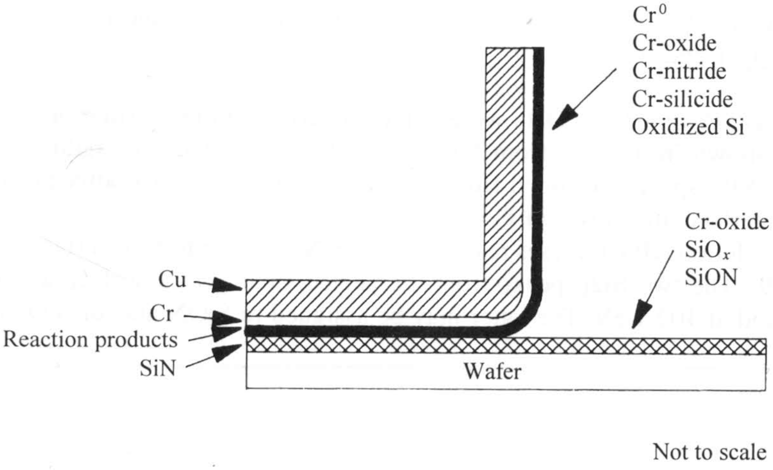

Figure 7. Schematic representation of the chemical species at the locus of failure for Cr/SiN.

SiO_x assignment is unlikely since the O1s found at 531.1 eV is about 1.4-2.6 eV below the expected O1s BE for Si-oxides [31]. This O1s is likely to be associated with Cr. The N1s peak at 396.9 eV is assigned to Cr-N species [31]. Since the N1s peak BE for SiON is 398.4 eV [32], it is not clear which Si-species corresponds to the Si2p peak at 102.1 eV. The lower BE Si2p peak at 99.3 eV may be due to Si^0 or silicide [31]. If elemental Si is formed on the Cr interface surfaces, it would oxidize upon exposure to ambient conditions (Table 2), whereas silicides are stable in air and do not oxidize at the ambient temperatures [45]. The low BE Cr2p peak at 574.0 eV supports silicide formation, but this peak may also be due to elemental Cr. The latter interpretation of the Cr2p data is reasonable since the deposited material is Cr^0.

On the substrate, Si is found in SiON and SiO_x forms based on the Si2p singlet at 102.1 eV, N1s at 397.8 eV, and O1s at 532.1 eV. The Cr found on the substrate interface surface is completely oxidized. Figure 7 gives a schematic representation of the suggested species present at the Cr/SiN locus of failure.

Both sides of the interface have Cr-oxide. Some Cr oxidized either during the initial stages of Cr deposition (base pressure of the deposition chamber was about 10^{-7} Torr), or during the peel experiment. The sputter deposited Cr has reacted with the treated SiN surface resulting in the Cr-oxides, -nitrides, and -silicides. The peel locus of failure is between this reaction products layer and the residual treated SiN layer. The Cr-oxide on the substrate side is either due to the Ar-ion sputtering (see Table 6) and/or the Cr metal deposition.

The SiN surfaces in this study do not contain Si_3N_4, but Si$-$0 as well as Si$-$0 bonds are present (Fig. 4 and Table 6). The reduction of Si_3N_4 and SiO_2 by the metals may be used as a guide to gain understanding of the metal/SiN interfaces. The standard free energy, ΔG^0, of SiO_2 reduction by the metal, as in the reaction;

$$\frac{5}{2}\,SiO_2 + 2\,Ta \rightarrow Ta_2O_5 + \frac{5}{2}\,Si,$$

Table 10.
Heat of oxide and nitride formation as compared to standard free energy or heat of reaction of SiO_2 or Si_3N_4 reduction

Metal	Oxide/nitride	Heat of formation (kJ/mol)	Standard free energy of SiO_2 reduction (kJ/mol)	Heat of reaction of Si_3N_4 reduction (kJ/mol)
Ta	Ta_2O_5	−2046	+223	—
Cr	Cr_2O_3	−1140	+223	—
Si	SiO_2	− 908	—	—
Ta	TaN	− 251	—	−65
Cr	CrN	− 125	—	+61
Si	Si_3N_4	− 743	—	—

and the heat of reaction ($\Delta H^0 \approx \Delta G^0$) of Si_3N_4 reduction by the metal, as in the reaction;

$$\frac{1}{4}\,Si_3N_4 + Ta \rightarrow TaN + \frac{3}{4}\,Si,$$

are compared with the heat of metal oxide and nitride formation[1] in Table 10.

The positive heat of reaction ($\Delta G^0 \approx \Delta H^0$) in Table 10 for Cr suggests that Cr cannot reduce SiO_2 or Si_3N_4. On the other hand, Si_3N_4 reduction by Ta is thermodynamically feasible. Therefore, thermodynamically Cr should not adhere well to either surface, while Ta should adhere well to Si_3N_4 surface. Based on the positive heat of reaction, Cr should not reduce Si_3N_4. However, CrN species are detected on the metal peel interface surface of the Cr/SiN system suggesting that a reaction between Cr and the treated SiN surface has occurred. Even though CrN formation in this system is thermodynamically not feasible, it is apparent that the system has enough energy to cause this reaction to occur. This may be due to the reactive surface created by *in-situ* Ar-sputtering (for example, ions, radicals) and/or the sputter deposition of Cr. Notice also that both TaN and CrN species are found on SiN surface after exposure to Ar-sputtering (Section 3.1.4.).

3.2.3. Cr/SiO_2 and Ta/SiO_2 interfaces. The Si at a Si2p BE of 99.3 eV, presumably due to Cr-silicide, is present at the Cr/SiO_2 metal (Fig. 8A), but not at the substrate peel surface. The Si2p peak at 99.3 eV is absent from the Si2p spectrum from the Ta peel surface of peeled Ta/SiO_2 interface (Fig. 8B). Table 11 is a summary of XPS data obtained from Cr/SiO_2 and Ta/SiO_2 locus of failure studies. In the Ta/SiO_2 system, as with Cr/SiO_2, the LOF is between the reaction products layer (SiO, Ta-oxide) and the SiO_2 (Si2p at 103.4 eV). The presence of Ta-oxide on the substrate side is due to the Ar-sputter cleaning and/or Ta sputter deposition processes.

The presence of SiO_x species on the peel interface surfaces of both Cr/SiO_2 and Ta/SiO_2 is supported by the following LOF findings:

- Si2p BE of 102.1–102.4 eV is due to SiO_x [31, 32].

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[1] Suggested by reviewer.

- The O1s BE at 532.3 eV is consistent with Si−O bonding [31], in either SiO_x or SiO_2. Since the Si2p BE is significantly less than 103.7 eV, the BE for SiO_2, suggesting that the Si species on the metal peel interface surface are from SiO_x. The O1s peak in Cr/SiO_2 is at 531.9 eV, which is somewhat lower BE than expected for SiO_x.

In the Cr/SiO_2 system the locus of failure observed after peel testing occurs between the layer of reaction products (Cr-silicide and SiO_x) and SiO_2 (Si2p at 103.1 eV) as shown in Fig. 9. The presence of Cr-oxide on the substrate side is either from the Ar-sputter cleaning and/or Cr sputter deposition processes.

Figure 10 shows results of the analysis of LOF data for the Ta/SiO_2 system.

In both SiO_2 systems the failure is interfacial in that it occurs between the reaction products layer and the substrate, so that SiO_2 is found only on the substrate surface. The difference between Cr/SiO_2 and Ta/SiO_2 peel strengths is insignificant since the peel strengths are very low. The low peel strength data suggest that the magnitude of the heat of oxide formation [9] cannot be used directly as a criterion for good adhesion. A better measure of interfacial interaction may be the standard free energy of metal oxidation by the underlying SiO_2 (Table 10). Although the heat of oxide formation is high for Ta and Cr [9], thermodynamically neither Ta nor Cr should

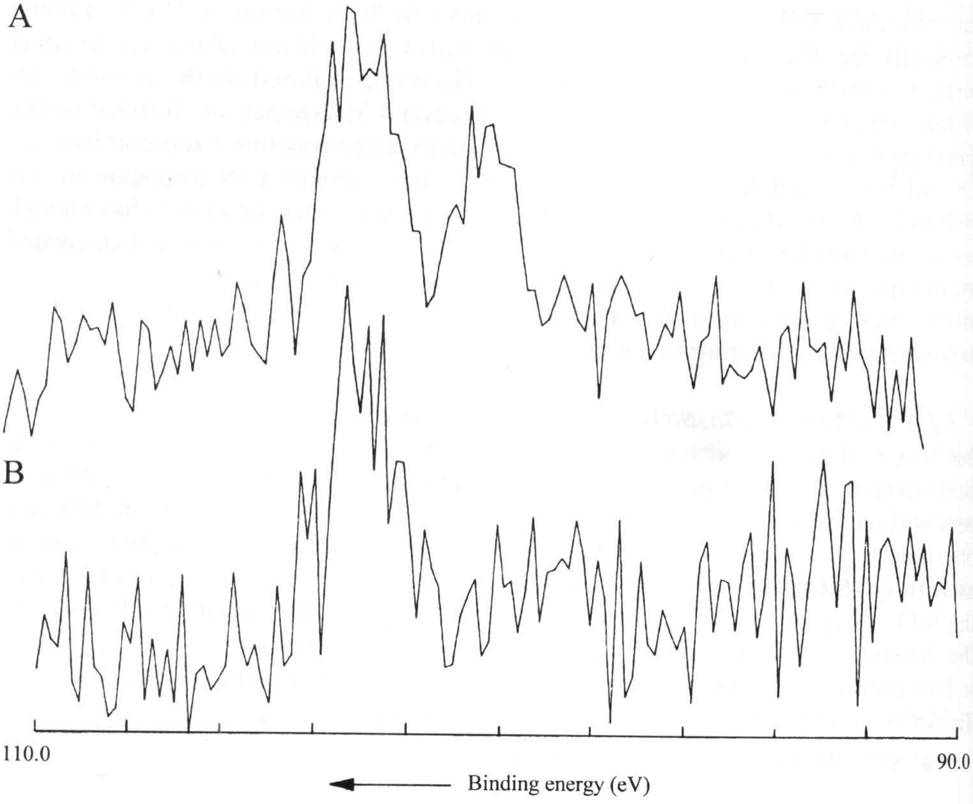
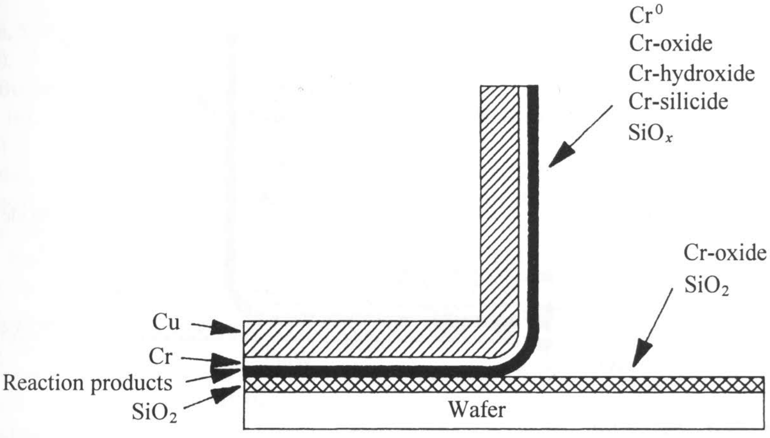


Figure 8. XPS Si2p peaks for A) Cr/SiO_2 and B) Ta/SiO_2 peeled metal interface surface.



Not to scale

Figure 9. Schematic representation of locus of failure for Cr/SiO_2.

Table 11.
Cr/SiO_2 and Ta/SiO_2 XPS locus of failure analysis results

Interface	Peel interface surface	Element	Observed BE (eV)	Literature BE (eV)	Literature assignment	References
Cr/SiO_2	metal	O1s	530.5	530.0–530.8	Cr-oxide	[31]
			531.9	531.2	$Cr(OH)_3$	[31]
				532.5	−Si−O−	[31]
		Si2p	99.3	98.9–99.7	Si^0	[31]
				99.4–100.5	silicide	[31]
			102.1	102.0–102.7	−Si−O−	[31]
		Cr2p	574.0	573.8–574.7	Cr^0	[31]
			576.3	575.9–576.8	Cr-oxide	[31]
	substrate	O1s	532.2	532.5	−Si−O−	[31]
		Si2p	103.1	103.0–104.0	SiO_2	[31]
		Cr2p	576.9	575.9–576.8	Cr-oxide	[31]
Ta/SiO_2	metal	O1s	530.8	530.6	Ta_2O_5	[31]
			532.2	532.5	−Si−O−	[31]
		Si2p	102.4	102.0–102.7	−Si−O−	[31]
		Ta4f	21.4	21.8	Ta^0	[39]
			26.6	26.5–26.9	Ta_2O_5	[31, 39]
	substrate	O1s	532.7	532.5	−Si−O−	[31]
		Si2p	103.4	103.0–104.0	SiO_2	[31]
		Ta4f	23.4	24.0	TaO	[39]
			25.9	26.0	TaO_2	[39]
			27.9	27.0	$TaSi_2$	[31]
				26.5–26.9	Ta_2O_5	[31]

adhere well to the SiO_2 surface (Table 10, positive ΔG^0 of SiO_2 reduction by Ta or Cr), which is supported by the study presented.