

SPECIAL SERIES ON IRRADIATION-ENHANCED ADHESION

Ionizing beam-induced adhesion enhancement and interface chemistry for Au–GaAs*

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MeV ion beam-induced adhesion enhancement of Au-films (~500 Å thick) on p-type and n-type GaAs substrates has been studied by the scratch test, ESCA, and nuclear reaction hydrogen profiling. For films resistively deposited in a diffusion pumped chamber at $2\text{--}5 \times 10^{-6}$ torr, the data indicate that the adhesion enhancement is associated with oxide layers on the substrate surface adsorbed before the film deposition. The ESCA data suggest that water vapour dissociates and forms $\text{Ga}(\text{OH})_3$ at the interface layers under ionizing radiation. The oxide concentration at the interface varies with substrate electronic properties and gives a large difference in the adhesion enhancement. However, the data obtained so far on the hydrogen concentration at the interface indicate that within our range of sensitivity it is about the same for substrates with different electronic properties. Our data demonstrate the importance of a thin adsorbed (impurity) layer for the interface chemistry and adhesion enhancement by ionizing radiation.

1. Introduction

The first use of an ionizing radiation in producing adhesion enhancement of thin metallic films to various substrates was by Griffith, Qiu and Tombrello at Caltech¹. Since that discovery there have been extensive experimental efforts (to clarify the physical mechanism) involving MeV ions^{2,3}, keV electrons^{4,5} or UV photons⁶ as the ionizing radiation. The proposed mechanisms are ionization-induced atomic mixing^{1,7}, an electrostatic mechanism due to the charge distribution at the interface⁸, and new bond formation for the ionization-induced interface chemistry⁹. Among these the last process, i.e. new bond formation from the induced interface chemistry seems to be most plausible based on the experimental data published so far.

Ionizing radiation can enhance a chemical reaction at a gas–solid or liquid–solid interface. For example, the irradiation of

solid surfaces by UV photons enhances the etching rate of gas phase or liquid phase etchants on GaAs and Si^{10–12}. The etching rate is believed to be enhanced by photochemical gas-phase photodissociation and combined surface- and gas-phase chemistry in the dry etching case. In addition, irradiation of GaAs by 4 keV electrons in an oxygen pressure of 5×10^{-5} torr triggers gallium oxide formation at the surface¹³.

Chemical methods for cleaning substrate surfaces prior to film deposition are usually not capable of preventing the surfaces from adsorbing monolayer films of water or carbon compounds¹⁴. Also, a cleaned surface rapidly becomes covered when exposed for even a short period to the atmosphere. These surface contaminants that adsorb from the atmosphere or remain after the chemical cleaning can be removed from the surface prior to film deposition by raising the temperature of the substrate in vacuum or bombarding the substrate surface with high velocity ions.

If there exist impurity (oxide) layers at the film–substrate interface, then an ionizing beam-induced chemical reaction is likely to take place between the impurity layer and the substrate interface or the thin film interface. In this paper we present studies using ESCA of the beam-induced interface chemistry for MeV-ion-bombarded Au films on GaAs substrates¹⁵.

*Supported in part by the National Science Foundation (DMR83-18274) and the IBM Corporation.

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2. Experimental

GaAs wafers with four different dopants (Cr, Si, Te and Zn) were used in the present study. The wafers were chemically cleaned prior to the film deposition by the following procedure: wash in Alconox detergent and warm water in an ultrasonic bath, rinse in deionized water and in methanol, etch in a solution of 3-5 drops of bromine in 100 ml methanol for about 5 min, rinse in methanol, and blow dry with dry nitrogen. The cleaned wafers were loaded into a diffusion-pumped bell jar in which the wafers were pumped on for 2-5 h before the film evaporation. Gold films (~500 Å thick) were deposited by resistive heating at $2-5 \times 10^{-6}$ torr. The samples were then irradiated with Cl or F ions in the energy range of 2-18 MeV.

Bombarded samples were tested with the scratch test⁸ and with ESCA. A HP5950A ESCA spectrometer with monochromatic AlK α (1486.6 eV) radiation was used. For the ESCA measurements, the Au films were chemically removed with a dilute solution of KCN in H₂O prior to loading into the ESCA chamber, because the escape depth of the photoelectrons is only 10-20 Å¹⁶. Hydrogen at the interface of as-deposited samples was investigated with nuclear reaction hydrogen profiling, which measures the H by a resonant nuclear reaction, i.e. by $^{19}\text{F} + ^1\text{H} \rightarrow ^{16}\text{O} + ^4\text{He} + \gamma$ at a bombarding energy of 6.42 MeV.

3. Results

The results of the scratch test are given in Figure 1 for the four different GaAs substrate samples bombarded with 18 MeV Cl ions. The bottom of the bars indicate the load (on the 1 mm scratch ball tip) at which the Au film starts to be partially removed and the top of the bars indicate the load at which the film is totally removed. The unbombarded films could be removed at 5 g, the lowest weight used. The two n-type, Si- and Te-doped, samples behave very similarly, i.e. negligible adhesion enhancement for doses below 10^{14} cm⁻². The Cr-doped semi-insulating GaAs sample shows a substantial increase in adhesion for low bombardment doses ($< 5 \times 10^{13}$ cm⁻²). On the other hand, the Zn-doped p-type conducting sample does not exhibit any significant enhancement even for high beam doses.

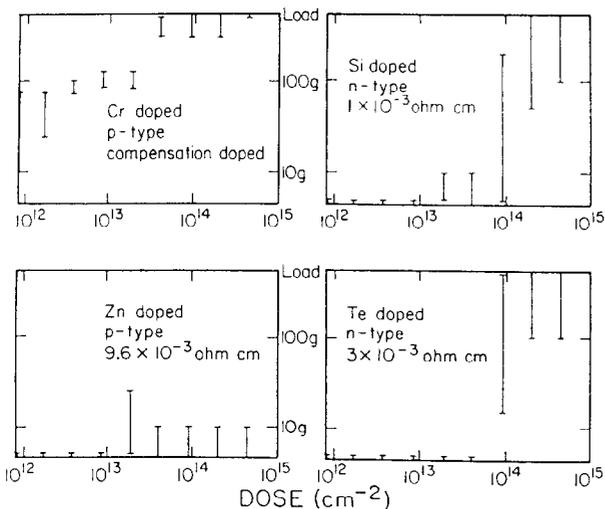


Figure 1. Plot of scratch test load that causes film stripping from a GaAs substrate. The bars indicate the load range, from initiating of partial stripping (bottom of bar) to total stripping (top of bar).

Figure 2 shows the oxygen concentration at the GaAs substrate surfaces (stripped of Au films by KCN etching) as a function of sputtering time with 1 keV Ar ions. Two bombarded (3×10^{14} cm⁻² of 18 MeV Cl ions) Zn-doped and Si-doped substrate samples and one unbombarded Si-doped sample were investigated with ESCA. The ESCA experiment was performed on the surfaces of as-stripped samples, and after subsequent sputtering with Ar ions.

It can be seen in Figure 2 that the O 1s peak heights, after a few minutes of sputtering to remove the contamination due to the Au film removal, are correlated with the scratch test results given in Figure 1. The bombarded Si-doped substrate requires a sputter time roughly twice as long as that for the unbombarded Si-doped substrate for the oxygen peak heights to be reduced to half the original values. For the bombarded Si-doped and Zn-doped substrates, the Si-doped sample has a higher oxygen concentration at a given sputter time and the oxygen extends deeper into the substrate. It should be noted that the chemical cleaning and Au film deposition was done for all three samples at the same time and the *in situ* sputtering was performed simultaneously in the same Ar ion beam. Because the sputtering rate was not calibrated, however, there is no quantitative depth information.

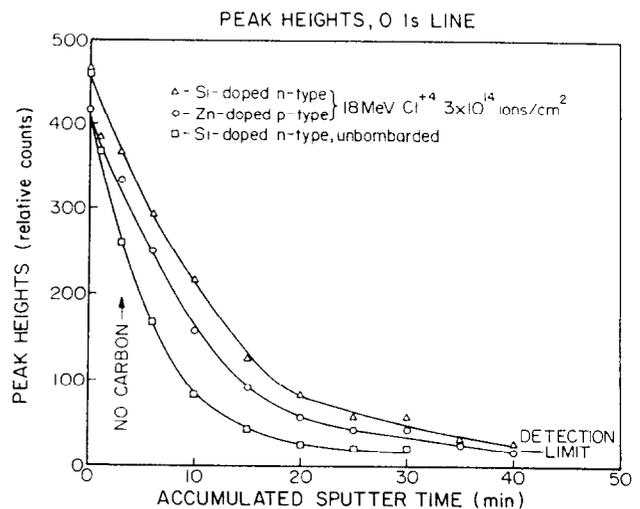


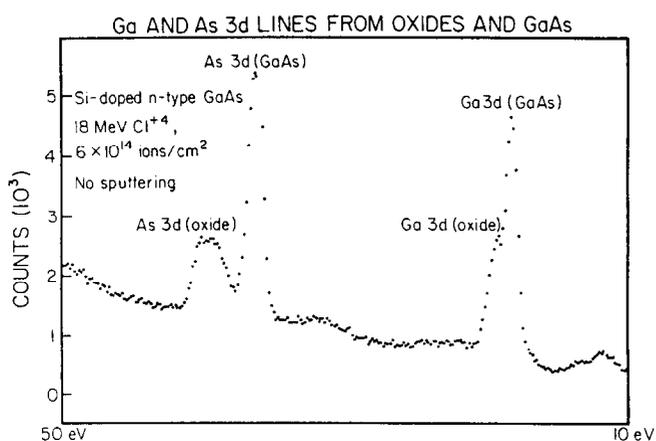
Figure 2. ESCA peak heights of the O 1s line as a function of sputtering time. The data compare the oxygen concentration for different substrates before and after the ion bombardment.

Figure 3 shows the Ga 3d and As 3d lines from oxides and GaAs on the surface of a bombarded substrate. This spectrum was obtained after the Au film had been removed in KCN solution and before the surface was sputtered with Ar ions in the ESCA chamber. The figure shows that the lines from oxides and GaAs are resolved from each other for As 3d but not for Ga 3d. However, since the arsenic oxides dissolve in water while the gallium oxides do not, the arsenic signal from oxide is believed to arise from the native oxides formed after the Au film had been etched off.

Table 1 gives the peak heights of As 3d, O 1s and C 1s lines as a function of increasing sputter time. The information on Ga 3d peak heights is not given because the Ga 3d line from GaAs is not resolved from that of the oxide. The contamination on the substrate surface, i.e. the arsenic signal from oxides and the

Table 1. Peak height data for bombarded and unbombarded GaAs substrates with different dopants

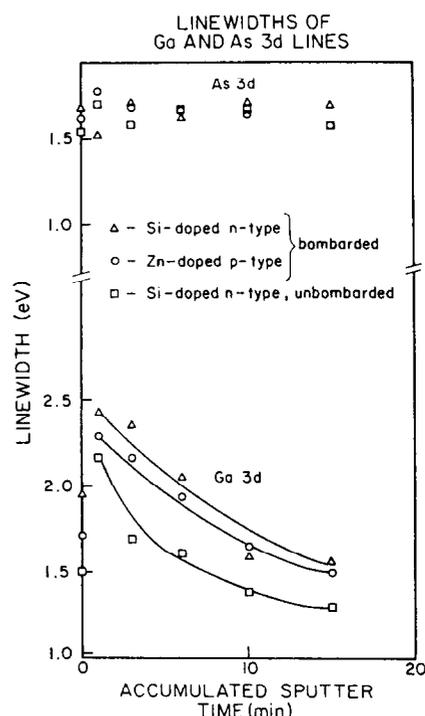
Sputter Time (min)	Si-doped n-type GaAs (accumulated 18 MeV Cl ⁺ , 3 × 10 ¹⁴ cm ⁻²)				Zn-doped p-type GaAs (18 MeV Cl ⁺ , 3 × 10 ¹⁴ cm ⁻²)				Si-doped n-type GaAs (unirradiated)			
	As 3d (GaAs)	As 3d (Oxide)	O 1s	C 1s	As 3d (GaAs)	As 3d (Oxide)	O 1s	C 1s	As 3d (GaAs)	As 3d (Oxide)	O 1s	C 1s
0	193	93	467	110	200	70	417	90	230	72	460	104
1	277	75	383	36	260	50	367	24	323	25	367	15
3	313	27	367	0	327	20	333	0	375	0	260	0
6	342	0	293	—	340	0	250	—	400	0	167	—
10	342	0	217	—	358	0	158	—	383	0	83	—
15	353	0	127	—	403	0	92	—	408	0	43	—
20	—	—	83	—	—	—	58	—	—	—	≈ 25	—
25	—	—	57	—	—	—	42	—	—	—	≈ 20	—
30	—	—	58	—	—	—	42	—	—	—	< 20	—
35	—	—	≈ 30	—	—	—	≈ 25	—	—	—	—	—
40	—	—	< 25	—	—	—	< 17	—	—	—	—	—

**Figure 3.** ESCA spectrum for Ga 3d and As 3d lines. Oxide satellite signal is resolved for As, but not for Ga.

carbon signal, formed after the Au film removal, is seen to be all removed by 6 min of sputtering. Thus, the GaAs surface is regarded to be free of post-etch contamination after 6 min of sputtering.

The linewidths of the As 3d and Ga 3d lines are presented in Figure 4 as a function of sputter time for the same samples as shown in Figure 2. The higher the oxide concentration, the larger the linewidths of the Ga 3d line. The Ga 3d linewidths (FWHM) data are consistent with the oxygen concentration data (see Figure 2) and the scratch test results (see Figure 1). This is evidence that the ionizing radiation (MeV ions in this case) induces the formation of oxides at the substrate surface.

Rough chemical compositions were obtained from the peak height measurements for the Si-doped substrates. After 6 min of sputtering when the post-etch contaminants of oxygen and carbon have been removed (see Table 1), the atomic percents are 32% As, 41% Ga and 27% O for the bombarded substrate, and 39% As, 45% Ga and 16% O for the unbombarded substrate. The relative oxygen concentration in the bombarded substrate has increased by MeV-ion-irradiation from that in the unbombarded substrate. Since there are no arsenic oxides left after 6 min of sputtering (see Table 1), these data suggest that the dominant Ga oxide is Ga(OH)₃ rather than Ga₂O₃ since after subtracting all Ga present as GaAs the ratio of O to the remaining Ga is 3:1.

**Figure 4.** Linewidths at half peak height vs sputtering time for Ga 3d and As 3d lines.

Therefore, the ESCA data suggest that the ionizing effects of MeV ions cause the impurity oxides at the film-substrate interface to diffuse more into the substrate and to be more strongly bound to the substrate atoms, which makes it harder to sputter off the oxygen atoms.

The hydrogen at the film-substrate interface was measured for the as-deposited samples by hydrogen profiling using the tandem accelerator at Caltech. The nuclear reaction for the hydrogen measurements, i.e. $^{19}\text{F} + ^1\text{H} \rightarrow ^{16}\text{O} + ^4\text{He} + \gamma$, has several resonances. We used the lowest resonant energy of the incoming ^{19}F ions in the present study (6.42 MeV), and the photons (γ) in the energy range of 6.1–7.1 MeV were measured by a NaI(Tl) detector.

Peaks in the γ -ray yield were observed for the ^{19}F energies corresponding to the resonant energy (6.42 MeV) at the surface of

the Au film and at the film–substrate interface. However, the relative heights of the interface peaks among the samples with four different substrates were not very reproducible for samples prepared at different times. The data obtained so far indicate that the interface hydrogen concentration is about the same for all four different samples deposited with the Au films in a diffusion pumped bell jar at $2\text{--}5 \times 10^{-6}$ torr.

More quantitative measurements of the interface hydrogen concentration for samples prepared in the above vacuum condition and in an oil-free uhv chamber are under way.

4. Discussion

In this paper we report that the impurity oxide layer at the interface has a major effect on the adhesion enhancement and interface chemistry induced by ionizing radiations. From our data, the water vapour adsorbed on the substrate surface plays an especially effective role among the impurities (such as hydrocarbons) in the radiation-affected interface processes.

It is noted that preparing an impurity-free interface to a sub-monolayer level is critical for studying the ionizing beam-induced interface chemistry and adhesion enhancement. In this regard, we are continuing our study in an oil-free uhv chamber, which has the capabilities of *in situ* evaporation, irradiation and substrate heating to desorb the water vapours from the substrate surface before film deposition.

For the systems prepared as in the present study, the ionizing beam-induced adhesion enhancement seems to be due to the combined effect of the molecular dissociation of impurities and the electronic excitation of the interface atomic layer(s) of substrate and perhaps the thin film as well. Our data also indicate that interface oxygen migration is caused by the ionizing radiation.

In our case, the results are consistent with a model in which the adsorbed water vapour at the Au–GaAs interface dissociates (and diffuses more deeply into the substrate) and forms new compounds with Ga (and As) in the surface layers of the substrate. The radiation-induced interface chemistry between the thin film and the impurity species at the interface needs further study. The

different enhancement in adhesion for substrates with different dopants (or electronic properties) seems to be due to the different amounts of oxide on the GaAs substrates.

The oxygen migration into substrate surface layers is another interesting electronic ionization induced atomic process. The ionization effects of radiation damage in the production, migration and annealing of atomic defects in semiconductors have been previously studied.

As a final remark, the adhesion enhancement is to be studied from a view-point of interface chemistry induced by various ionizing radiations. In systems with impurity oxides at the interface, the oxide chemistry seems to control the adhesion enhancement. For a better understanding of related physical processes, the preparation of an impurity-free interface seems to be essential.

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