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DEPOSITED ALUMINUM FILMS

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ABSTRACT

RATE AND PRESSURE DEPENDENCE OF CONTAMINANTS IN VACUUM DEPOSITED ALUMINUM FILMS

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Experiments have been conducted to measure the quantity of trapped impurities in electron beam deposited aluminum films. The depositions were conducted at the 1.3×10^{-4} Pa to 1.3×10^{-2} Pa pressure range with rates varying from a few Å/sec to 70 Å/sec. An RGA was used to record the residual gas spectrum before and during all runs. The films were analyzed by sputter profiling and Auger Electron Spectroscopy. The chief contaminants found were carbon and oxygen. The carbon contaminant tracked the gauge pressure over two orders of magnitude ranging from a few atomic percent to the 500-1000 ppm range. The partial pressures of H₂O, O₂ and other gases were varied during deposition to determine their individual roles in contaminating the films. As a result, a relationship between the residual gas spectrum, and chemical analysis was found.

RATE AND PRESSURE DEPENDENCE OF CONTAMINANTS IN VACUUM DEPOSITED ALUMINUM FILMS

INTRODUCTION

The deposition of thin films by electron beam gun is usually carried out in vacuums ranging in pressure from 10^{-5} Pa to 10^{-2} Pa. Measurements of film properties such as intrinsic stress, electrical conductivity or hardness measurements are routinely made on these materials. Properties thus measured are usually ascribed as intrinsic to the structure; for example grain size variations with temperature. However, little note is usually given to the residual gases in the chamber during the deposition. This may be due to the lack of analysis capability and sensitivity of most chemical techniques when dealing with a few hundreds of micrograms of material or less.

The possibility that residual gases may play a significant role in both the structural and chemical properties of thin films is evident by considering deposition pressures and times giving one-Langmuir exposure. If the sticking probability of the gas adatoms were one, then a dose of one Langmuir (1.33×10^{-4} Pa-sec) would be sufficient to produce a monolayer. Under the preceding conditions, a deposit made at a few atomic layers per second could be quite impure. Thus, a correlation between measured residual gases, gauge pressure and sticking probability is desirable.

The simplest formulation for the computation of contaminants in a deposit is given in equation 1, where I_f is the total impurity fraction.

$$(1) \quad I_f = \sum_i K \lambda_i (\tau, \theta) \frac{R_{gi}}{R_d}$$

The equation describes the impurity in the deposit in terms of the rate of incident impurity (R_{gi}), the rate of deposit (R_d), the sticking probability λ_i , a scaling factor (K), and θ is the fraction surface coverage. R_{gi} may be computed from ideal gas theory and by using the partial pressure of the constituent as determined from a residual gas spectrum of the chamber. The rate of deposit (R_d) may be computed from the crystal structure by dividing the film step height by the time of deposition,

or by an in situ quartz crystal monitor. The sticking probability,

λ_i , is measured by a number of techniques. Among the more common methods is the preparation of a film under ultrahigh vacuum conditions followed by admitting the gas of interest at various pressures to the chamber while monitoring the adsorption. The method of monitoring can be the measuring of the shift in frequency of a quartz crystal coated with the film of interest, gas volumetric techniques, or signal strength changes in x-ray photoelectron spectra.⁽²⁻⁷⁾ These measurements usually produce the sticking coefficient as a function of temperature, T , and surface coverage, θ . The K represents a scale factor to compensate for the difference in location of the gas pressure measurements and the true gas pressure at the sample location. If all these parameters are known, estimates of film impurity can be computed.

The scope of this work involved measuring the contaminants due to residual chamber gases in aluminum films deposited at room temperature. The objective was to compare the measured impurity levels in films, deposited as a function of residual gas partial pressure and rate of deposition, with the ionization gauge pressure. The two measurements can then be related through equation 1.

EXPERIMENTAL

The films were all deposited from a 14 kW single hearth electron beam gun; the hearth had no liner. The aluminum used was 99.999% pure. To insure minimum carbon and oxygen contamination in the aluminum source material, the material was analyzed by conventional wet chemistry techniques. The carbon and oxygen levels were found to be less than 50 ppm each, including surface contamination. Thus, in addition to low metallic impurity levels, the aluminum was essentially free from carbon and oxygen.

The deposition chamber consists of a stainless steel chamber with a Pfeiffer turbomolecular pump. The speed of the pump is rated at 400 l/s for nitrogen. A typical ultimate pressure, with LN₂ in the Meissner trap, is $\sim 3 \times 10^{-6}$ Pa. The deposition rates were monitored by use of a quartz crystal monitor. The step height of the film was measured by the stylus technique. Using the film thickness and deposition time, the average rate of deposition was compared with the direct reading crystal monitor and found to be in reasonable agreement.

The deposition rate was maintained constant by monitoring the ion current produced close to the source. The signal was amplified and fed back to the emission control.

The gases admitted to the chamber were oxygen, nitrogen, methane, carbon monoxide, and carbon dioxide. They were all 99% pure. The residual gas analysis showed that the other gases appeared to be mainly argon with trace amounts of CO and N₂. The water source was made by freezing about 1 cc of distilled water in the end of a sealed tube immersed in a liquid nitrogen bath. The tube was subsequently pumped out to high vacuum conditions. The liquid nitrogen bath was then removed and the ice allowed to thaw. As the chamber pressure rose, the leak valve was closed. After the water returned to the liquid state, an analysis for purity was carried out. The residual gas analysis showed an initial burst of oxygen and nitrogen followed by essentially 99% water vapor.

The gases were admitted to the chamber using a variable leak valve through a port in the base plate. The quadrupole mass analyzer, a UTI 100 C, was mounted adjacent to this port on the base plate. To minimize correction to any measured gas spectra the Faraday cup was used on all current measurements. The analyzer transmission is flat to about mass 50, so no correction was required for measured currents.⁽⁸⁾ In addition, the ionization efficiency for these gases is about the same, so no correction was required.⁽⁸⁾ The ionization gauge readings and mass analyzed ion current were directly proportional for single gas pressures of $\sim 8 \times 10^{-4}$ Pa to $\sim 2.6 \times 10^{-2}$ Pa. Above 2.6×10^{-2} Pa, only the ionization gauge pressure could be used as the maximum useful operating pressure of the quadrupole was exceeded. All spectra were measuring using a log amplifier output to facilitate analysis. The amplifier was useful in compressing ~ 4 decades, thus the same current scale was used for all spectra.

The substrates were glass microscope slides mounted on a large stainless steel plate. The temperature during the depositions was between 293 K and 303 K.

The chemical analysis was carried out using a PHI 545 Scanning Auger Microprobe. The base pressure before analysis began was $\sim 8 \times 10^{-9}$ Pa.

It was necessary to keep the liquid nitrogen trap on the sublimator charged in order to minimize carbon and oxygen contamination from the residual gases during the sputtering and analysis of the samples. The Auger analysis was made with currents ranging from 0.5 μ A to 5 μ A at 10 kV. The depth profiling was done with argon at 5 kV. The spectral measurements were signal averaged during the sputtering of the samples. A minimum of two sets of 64 scans were made on each sample for low carbon, oxygen and nitrogen measurements. The scans were compared to insure stability of the measured peak heights. Comparisons of elemental ratios showed no noticeable electron beam current effects in the range used. The ratios of the elements were found from equation 2, where S is the sensitivity factor for the elements.⁽⁹⁾

$$(2) \quad I = \frac{A_{pk-pk}}{\theta_{pk-pk}} \times \frac{S_0}{S_A}$$

This allows direct comparison with equation 1.

Detectability was not a problem because the signal averaging technique was used. Contamination from the analysis chamber was the chief limiting factor in the carbon measurement. The carbon could not be completely sputtered away on a pure aluminum button of source material. Thus, the limit for the carbon measurement was ~ 500-1000 ppm. The minimum measurable oxygen concentration was 100 ppm, and the limit on the nitrogen measurement was 100 ppm.

RESULTS AND DISCUSSIONS

A total of 45 aluminum films were prepared in varying residual gas atmospheres. For each gas, six samples were made. The typical thickness was ~ 1 μ m.

In initial experiments the residual gases in the chamber were varied by throttling the system gate valve. The residual gas spectra indicated a few principal gases that appeared to track the gauge pressure. These gases were hydrogen, water, carbon monoxide/nitrogen, and carbon dioxide. In addition, there were many peaks between mass 50 and 100 that were ~ 50 times weaker than the principal constituents. These peaks tended to

track the gauge pressure slower than the main gas components. The results of the Auger analysis of the deposits prepared with just the residual gases in chamber are shown in Fig. 1. The results include samples where both the rate and pressure were varied. The solid line is best experimental fit. The carbon variation was smaller than would be expected from equation 1 as the slope of the plot is less than unity. There does appear to be a contamination dependence on the residual gases in the chamber, although it is quite low.

O₂ VARIATION

The oxygen peak in the residual gas analysis was quite low and allowed for large variations. Some question about the oxygen results at low partial pressures could be raised due to the high $\frac{H_2O}{O_2}$ ratio. However, since the lowest partial pressure of oxygen was comparable to the water, it would likely only affect the results by a factor of 2 at this pressure range.

It is interesting to note that the appearance of the films varied with the oxygen concentration. The films prepared at low concentration had a milky appearance which had been noted by other workers.⁽¹⁰⁾ As the partial pressure increased, the milky appearance diminished with the films becoming shiny, turning dark, and finally almost transparent at very high partial pressures.

The results of the oxygen analysis are shown in Fig. 2. A plot of both the ionization gauge pressure and of ion current at mass 32 is shown. The inset at top shows a typical gas spectrum during one of the runs.

Numerous workers have measured the sticking coefficient for oxygen on aluminum films and bulk samples. The mechanism appears to be physisorption followed quickly by chemisorption. Work function measurements indicate that there is probably reconstruction at the surface as shown by a drop in the work function.⁽⁶⁾ This is explained in terms of the dipole theory with the positive ion on the surface. The absolute measured value of the sticking probabilities varies somewhat, but all

measurements show that it remains essentially constant for a coverage of $\theta \sim 1$, at which point it falls off dramatically. The value for the sticking coefficient of 0.03 measured by Kreuger et al.⁽³⁾ is typical. Using this sticking coefficient and a scale factor of ~ 2 , equation 1 is plotted in Fig. 2. The agreement between the experiment and the calculation is reasonable.

H₂O VARIATION

The range of partial pressures investigated for the water is similar to the oxygen. The films tended to show the same appearance changes as with the oxygen variation. The total transparency of the film deposited at the highest water partial pressure was extremely striking. The residual gas spectrum showed the chamber to be chiefly hydrogen during all runs. This is easily observed by comparing the current scales of the mass spectrum in Fig. 3 (showing the oxygen to aluminum ratio for water) to that in Fig. 2. Evidently the hydrogen evolution indicates a cracking of the water molecule at the surface of the fresh film deposit.

The product of this water dissociation is thought to be a mixture of oxide and hydroxide. This is the conclusion of an XPS measurement of the oxygen line shape of water adsorbed on aluminum films made by Fuggle et al.⁽⁵⁾ The experiment begins with water adsorbed on an aluminum film at 77 K. The oxygen line is indicative of the water. Upon warming to room temperature, the line shifts to the oxide position but remains considerably broader than the pure oxide, which is attributed to the hydroxide. Kreuger et al.⁽⁴⁾ have measured the room temperature sticking probability for water and found it to be 0.05.

Using equation 1, the Krueger sticking probability and the scale factor ~ 2 , the result is plotted in Fig. 3. The computation again agrees reasonably well with the measurement.

NITROGEN VARIATION

The pressure of nitrogen was varied from 10^{-5} Pa to 7×10^{-2} Pa. The films all had approximately the same appearance except for the noticeable scattering around the substrate clamps for films deposited at higher pressures. Only three of the films were examined for nitrogen

concentration. They were deposited at 4×10^{-3} Pa, 10^{-2} Pa, and 6×10^{-2} Pa. Figure 4 shows the results. The measured N/Al ratio in all cases was $\sim 5 \times 10^{-4}$.

This strange result can be explained by the sticking probability measured by Mayer et al.⁽⁷⁾ For liquid nitrogen temperatures the measured sticking probability is quite high, ~ 1 ; however, at room temperature it is $\sim 10^{-3}$ for initial coverage. As the coverage proceeds to $\sim 10^{-12}$ molecules/cm², the probability falls to $\sim 5 \times 10^{-5}$. This low value of the sticking probability reflects the fact that the nitride does not form at room temperature. Evidently the dissociation energy is too high. Thus, for high gas pressure $\sim 4 \times 10^{-3}$ Pa, a saturation coverage of $\sim 7 \times 10^{11}$ molecules/cm² would be quickly established. Under these conditions, a constant ratio of 1.4×10^{12} atoms/cm² / 2.5×10^{15} atoms/aluminum layer = 5.6×10^{-2} atomic percent would be expected. The measured results of $\sim 5 \times 10^{-2}$ atomic percent are in reasonable agreement with this estimated value.

CARBON-BEARING GAS VARIATION

Methane, carbon monoxide and carbon dioxide were used because they were the principal constituents of the gas spectrum found in the initial residual chamber gas experiment. It was thought that these gases might contribute to the carbon measurement found in Fig. 1. The relative intensities of these gases were varied from 10^{-4} Pa to 10^{-2} Pa. Figure 5 shows the results obtained for these three gases. There was no noticeable difference in the value of the carbon measurement for any of these films. The analyzed value ~ 0.05 - 1 atomic percent is typical of the lowest values that could be obtained with this particular Auger system, and significantly overestimates the carbon content. In addition to the contamination problem, the estimates for carbon content would be in error for two additional reasons -- first, the line shape for the carbon is significantly different here than for the graphite reference used in obtaining sensitivity factors for data reduction; secondly, it is well known that different sputtering yields will cause a surface enrichment of the lower yield component. The enriched layer stabilizes in composition, under steady state conditions, to the inverse ratio of the sputtering

yield times the bulk composition.⁽¹¹⁾ Thus, with carbon being suspected of a lower yield than aluminum, any carbon measurement would be higher than the true bulk composition. However, an upper limit to the sticking probability of these gases can be estimated by using equation 1, the 0.1 atomic percent carbon level and the highest gas pressures used, $\sim 66 \times 10^{-2}$ Pa. Under these conditions, the sticking probability for any of these gases at room temperature must be less than $\sim 5 \times 10^{-5}$.

Metallurgical data⁽¹²⁻¹⁴⁾ for the interaction of carbon or the carbon-bearing gases with aluminum is scant. Reports of sticking coefficients for these gases could not be found. However, the little data found indicates that reactions with CO and CO₂ can be produced forming various mixtures of oxide and carbide but not below 1100 K and 950 K respectively. However, the details of these measurements were not given and it is not known if a protective oxide may have altered the results. Nonetheless, these results would indicate that room temperature interaction with these gases would be very small as observed.

CONCLUSION

The contamination of aluminum films deposited by electron beam gun at room temperature over a wide range of residual gas pressures has been investigated. Of the gases investigated, only oxygen and water showed any significant chemical activity. Although these gases have sticking probabilities much less than unity, correlation between the residual gas measurement and ionization gauge pressure has been demonstrated. In general, the gases may be treated independently unless large concentrations of both are measured.

The sticking probability of water on an oxidized surface is reported to be higher by $\sim 3\times$ ⁽⁴⁾. Thus, the sticking probability for a partially oxide surface becomes $\lambda' \approx 3\theta\lambda + (1-\theta)\lambda$. As can be seen, unless approaches $\sim 10\%$ there is no significant adsorption enhancement.

The nitrogen sticking coefficient is quite low and is reflected in the extremely low measured value of nitrogen in the films.

The remaining gases - methane, carbon monoxide and carbon dioxide, appear to have vanishingly small sticking coefficients. Estimates for their sticking probabilities at room temperature must be less than 5×10^{-5} .

In conclusion, the carbon contamination must be due to the weak mass peaks above mass 50. The residual gas spectrum shows the disappearance of the weak peaks above mass 50 as the deposition progresses. The critical gases below mass 50 are water and oxygen. Thus, aluminum films relatively free from oxygen and carbon contaminant can be produced at room temperature by eliminating water, oxygen, and mass sources above mass 50.

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FIGURE CAPTIONS

Figure 1

The effect of throttling the system is shown in the graph. The solid dots were runs made at 70 A/sec. The open circle represents runs made at 7×10^{-4} Pa, but at 10, 30 and 40 A/sec. They have been corrected to the equivalent pressure for 70 A/sec.

Figure 2

The oxygen to aluminum ratio is shown for oxygen pressure variation. The solid points represent the data plotted as a function of RGA current. The triangles represent the data plotted as a function of gauge pressure. Note the multiplicity of data at the 10^{-3} Pa pressure. The squares represent runs made at ~ 6 times the 15 A/sec rate, and corrected for the increased rate. The inset displays a typical RGA plot for the data point indicated. Note that 32 and 16 are the major components.

Figure 3

The oxygen to aluminum ratio is plotted as a function of water pressure variation. The data represent the plot as a function of RGA current. The triangles represent the data plotted as a function of ion gauge pressure. Note the large difference in the scales of the pressure from Fig. 2. The difference can be seen in the RGA spectra as the hydrogen peaks are the major components.

Figure 4

The nitrogen atomic ratios are shown to be constant as expected from the variation in sticking coefficient. The RGA spectra shown is for the $\sim 2 \times 10^{-3}$ Pa run. Note the appearance of the peak at 14 verifying the presence of N_2 .

Figure 5

The plots of the three carbon bearing gases are shown here. The lack of variations in carbon is indicative of a very small sticking probability less than 5×10^{-5} .

Fig. 1

Fig. 2

Fig 4