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Stability of Gold Thin Films on Polyimide

G. Amoako^{1,2}, S. Y. Mensah¹, A. Twum, V. D. Teye

Abstract – Gold/Polyimide interfaces are prepared by depositing thin gold films onto polyimide with Si substrates and subsequently annealing at various temperatures. The interface is studied with the help of Rutherford backscattering spectroscopy. After deposition, different sample thicknesses exhibited different morphologies. High deposition rates resulted in the formation of gold islands. After annealing at higher temperatures polyimide covered the sample surface. Chromium was also used as a buffer between gold/polyimide interface to increase adhesion and possibly to decrease the tendency of gold to form islands and also to stop polyimide from covering the gold surface. To reduce the mobility of metal atoms, a gold film is prepared at $-68\text{ }^{\circ}\text{C}$.
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Keywords: Adhesion, Anneal, In-diffusion, Metal, Mobility, Morphology

I. Introduction

Metallized polymers are of considerable technological importance and are widely used for products ranging from reflectors for car lights, compact discs, and electrically shielded computer cases to foils for food packaging [1]-[2]. In almost all device geometries the metals are deposited on top of the polymer.

The investigation of metal/polymer interfaces offers a unique opportunity to study systems which are fundamentally challenging and yet provide information relevant to current device applications.

For actual and future technologies, there are bright prospects of fundamental and applied research on adhesion mechanisms between a metal and a polymer surface.

Since the last decade, the application of surface and interface analytical tools has succeeded in elucidating some aspects of the interface formation between a polymer and a metallic layer.

It has been shown that metals seldom bond to a polymer surface without undergoing some kind of chemical reaction.

As an example, a metal atom deposited by evaporation on an oxygen containing polymer generally interacts with the substrate oxygen and forms a metal-oxygen-polymer complex, which ensures a “good” adhesion of the two layers. For polymers without oxygen atoms, some metal bonding is still observed, as a result of a charge transfer from the metal to the polymer [3].

The continuous down-scaling of interconnect geometries will result in a drastic relative increase in propagation delay and power dissipation due to resistance-capacitance coupling problem, new materials of lower permittivity than SiO_2 (low-k materials) are needed if industry is to meet the high switching-speed requirements.

Because a primary concern in technological applications is the reliability of the device, a better understanding of the metal/polymer interaction together with the role the metal and the polymer play in the device contamination are needed. Further, the new dielectric materials must be consistent with processing temperatures and thermal conductivity requirements for heat transfer, both key issues that must be resolved before polymers are incorporated in future interconnect or other structures [4]-[6].

This work will study the stability of metal thin films (Au and Cr) deposited on polymer (PI). The metallization of the polyimide will be done at room temperature and at $-68\text{ }^{\circ}\text{C}$. Au is widely used for contacting organic electronic devices and rather inert, hence, specific chemical interactions play a minor role [7]. For chromium metallization, there is general agreement that the metal interacts strongly and preferentially with the PI to form a sharp interface [4]. The background to this work has been captured in works by [1], [8]-[11]. These samples were given heat treatment at several temperatures and then studied using Rutherford backscattering spectroscopy (RBS). The paper will be organized in six sections as follows: Section (I) is introduction, Section (II) will comprise the Sample preparation, and the Experimental with Section (III) on the Analysis of experimental results. Sections (IV) and (V) will be on Conclusion and References respectively.

II. Sample Preparation and Experimental

II.1. PI Synthesis

The polyimide (PI) used was PI2611 from Du Pont. The polymer synthesis process consists of spin-coating the PI at 2000 rpm for 30s and then subsequent heating to achieve imidization. The first heating step at the first

ramp was at 200 °C for 30 min. in air and then 10 min. in N₂. Curing was accomplished at the second ramp by heating under N₂ to 365 °C for 60 min. The sample was then cooled to room temperature. The polyimide thickness was 3 μm for all the samples.

II.2. Metallization

The metallization was performed *in situ* in the scattering chamber at the pelletron laboratory at the Max Planck Institute in Stuttgart Germany by means of thermal evaporation in vacuum.

In this evaporation deposition method, the solid material (Au or Cr) was heated to sufficiently high temperatures until fusion by means of electric current passing through a tungsten coiled filament in which the metal is deposited.

This assembly was then shielded with aluminum foil to prevent the metal from depositing at the walls of the scattering chamber.

The evaporated metal then condensed onto the cooler substrate (polyimide).

The samples (with the exception of the cooled sample) were at room temperature during the evaporation but since the metals were heated during the evaporation process, the substrate temperature increased after the process.

The PI sample was placed on a holder in front of the heating coil to facilitate the deposition of the metal onto it as the metal is heated.

The heating was achieved by means of a 10A DC power supply which supplied the voltage and the current needed.

The thicknesses of metals deposited were determined by RBS with the aid of the XRUMP-Genplot Simulation and the ERDT softwares.

The ERDT software gives the effective rate of change of energy in keV with respect to thickness. All samples were prepared on Si substrates of about 4000 nm.

The Rutherford backscattering spectroscopy data were taken at the Stuttgart Pelletron with He⁺⁺ ions of 1 MeV and a scattering angle of $\theta = 38^\circ$.

For the temperature-dependent measurements, the samples were mounted on a heater in vacuum, annealed at a given temperature for 30 min., and measured *in situ* by RBS at each temperature indicated in the figures.

III. Analysis of RBS Measurements

Several samples of different thicknesses were prepared and used.

These were (a) 5 nm Au/PI, (b) 6 nm Au/PI, (c) 13.5 nm Cr/PI, and (d) 7 nm Au/PI prepared at -68 °C. The reported temperatures are accurate to $\pm 10^\circ\text{C}$ for all the samples.

III.1. 5 nm and 6 nm Au/PI Samples

These gold samples were prepared in the scattering

chamber at the Pelletron laboratory as already described. The metallized 6 nm gold sample was heated *in situ* just after deposition to 90 °C, 160 °C, 255 °C, 345 °C, 400 °C, and 450 °C and annealed for 30 min. each at these temperatures.

The same treatment was given to the 5 nm gold sample but at temperatures of 85 °C, 125 °C, 200 °C, and 235 °C.

The RBS spectra of the 6 nm Au film are shown in Fig. 1a.

Fig. 1 shows the 6 nm gold sample annealed at different temperatures.

The surface of the sample corresponds to the right part of the spectra.

As evident from Fig. 1a the high energy edge shifts as the temperature increases from 90 °C to 450 °C towards lower energies.

Immediately after deposition the substrate temperature was 90 °C and the gold peak shows a sharp shape with a relatively steep high-energy edge and a much slower decay towards lower energies pointing to a rather rough surface structure of the film with perhaps some diffusion into the PI bulk.

Such a rough surface is also evidenced by Fig. 1b which presents an AFM image of the film which was taken after annealing. Annealing at different temperatures up to 450 °C shows no appreciable change in the peaks: the FWHM (9.8 keV) of the peaks stay almost the same. This indicates that the thickness profile changes only very little if any at all during annealing. The slight shift of the spectra from 160 °C to 255 °C indicates that some PI (maximum thickness: 0.62 nm) covers the surface of the Au apparently diffused through pinholes or along grain boundaries in the film to the surface. To provide more insight into the meaning of the spectra, Fig. 2 shows a comparison of one of the experimental spectra with an “ideal” spectrum, i.e. a spectrum simulated with the commercially available program RUMP for a sample with constant thickness, and with a simulated spectrum which fits the data well.

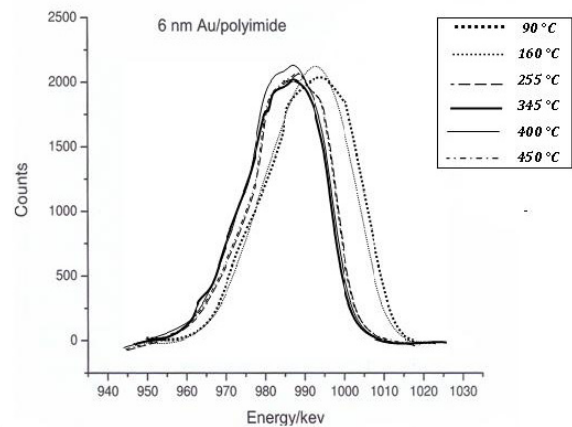


Fig. 1a. RBS spectra of 6nm Au /polyimide annealed at the temperature indicated in the fig. for 30 min each

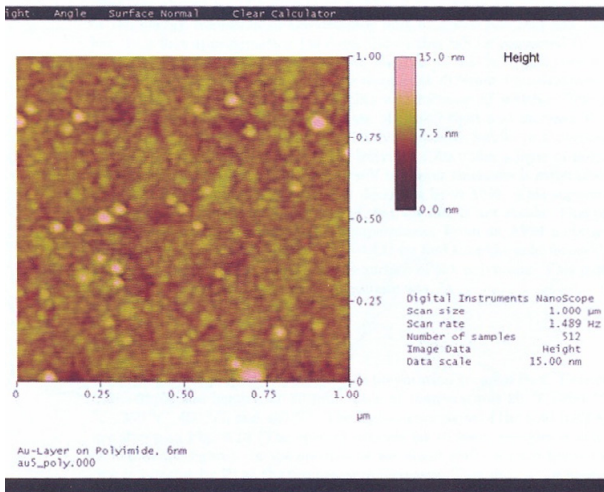


Fig. 1b. An AFM image of the film which was taken after annealing

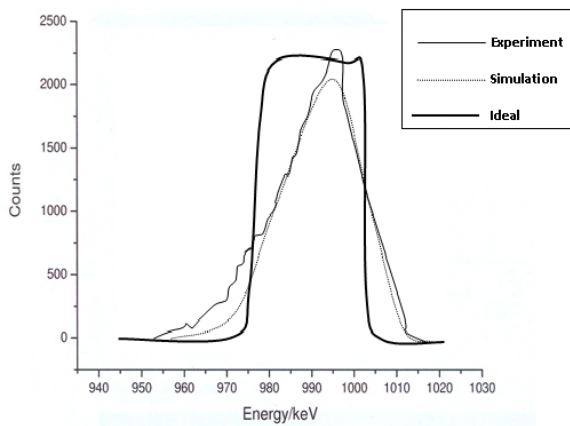


Fig. 2. Experimental RBS spectrum (90 °C) of Fig 1 and simulated one for 6 nm Au/polyimide sample. For comparison also an ideal spectrum shown as simulated for a film without surface roughness and no thickness fluctuations. The difference between the experiment and the ideal spectrum is due to a roughness of 9.8 keV corresponding to 2.2 nm

The high energy edge of the experimental spectrum in Fig. 2 shows that the surface of the sample is rough with a roughness of 9.8 keV corresponding to a thickness of 2.2 nm while the back edge indicates that there is a thickness fluctuation of about 4 nm in addition. We see from the AFM picture in Fig. 3 that the metal forms a large number of islands on the surface and according to [8] this inhibits diffusion of Au into the polymer.

Fig. 4 shows RBS spectra of the 5 nm Au/PI sample after annealing in the temperature range 85 °C to 235 °C. The high energy edge of this sample also shifts towards lower energies as the temperature is increased from 85 °C to 235 °C indicating that also in this case PI is increasingly covering the film surface.

The substrate temperature of the 5 nm sample was 85 °C immediately after deposition and the gold peak shows a relatively sharp shape with a steep edge at the high energy edge.

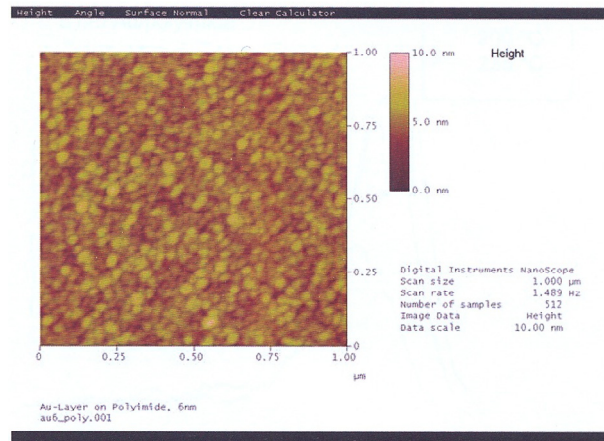


Fig. 3. AFM picture of the 6 nm Au/polyimide after annealing at the temperatures indicated in Fig. 1

Nevertheless, also in this case the sample exhibits some surface roughness that can be characterized by a Gaussian broadening of the edge by 12.8 keV as could be seen in the fit in Fig. 5. In a first approximation this can be converted into a mean roughness of 2.9 nm. Annealing this sample at different temperatures shows significant decrease in the peak heights and increase of widths. The higher the temperature, the larger the decrease of peak height and increase of width. Annealing at 125 °C for 30 min. already results in a marked shift towards lower energies suggesting the burying of Au under a layer of polyimide.

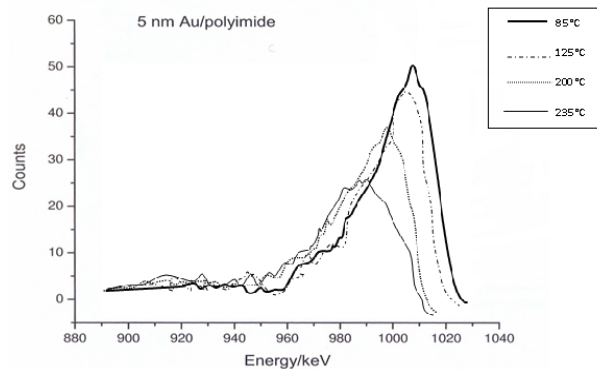


Fig. 4. RBS spectra of 5 nm Au/polyimide annealed at temperatures in the fig. for 30 min. each

According to the energy shift of 2.77 keV the layer thickness is estimated to be 0.62 nm. The maximum peak height decreases by $\approx 10\%$. This suggests that the Au film is decomposing, indicating that the film is not stable. This pattern continues after annealing at higher temperatures. From an AFM picture of the sample after heat treatment as shown in Fig. 6, it is found that the gold forms clusters and these clusters form islands on the surface of the polyimide essentially confirming the RBS measurements.

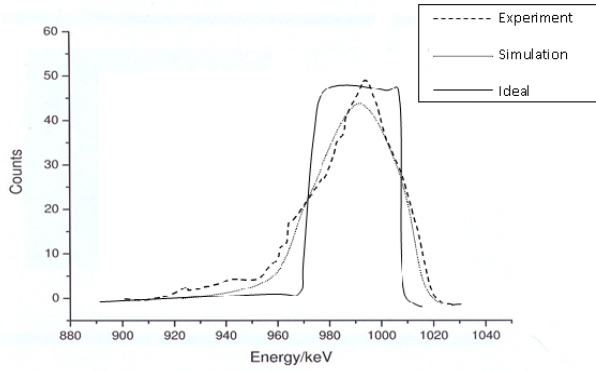


Fig. 5. Experimental RBS spectrum (85 °C) of Fig. 4 and simulated one for the 5 nm Au/polyimide sample. For comparison also an ‘ideal’ spectrum is shown, as simulated for a film without surface roughness and no thickness fluctuations. The difference to the ideal spectrum is due to a roughness of 12.8 keV corresponding to 2.9 nm

III.2. 13.5 nm Cr/PI Sample

Chromium was used as film material, since it is known to be highly reactive, and films of this material are expected to show a behavior different from gold. It has been argued that the data for PI do not imply reactive metals like Cr and Ti to be bonded directly to the polymer but rather suggest a disruption of the PI and the formation of oxidic, nitridic, and carbidic compounds [12]-[15]. A Cr film of 13.5 nm thickness was prepared and the sample annealed for 30 min. at temperatures 20 °C, 230 °C, 340 °C, and 440 °C. The spectra shown in Fig. 7 exhibit a smeared-out peak shapes with steep high-energy edges at all temperatures. Different from gold films the spectra show no shift of the high-energy edge upon annealing up to 340 °C. This is in line with Cr being more reactive than Au. Only after heating to 440 °C causes a small shift, indicating covering by small amounts of PI. Also the heights of the spectra are more or less the same, up to 340 °C. Only after annealing to 440 °C it decreases, apparently due to a higher amount of PI in the film region, probably caused by in-diffusion of PI into the film along pores or grain boundaries. The widths of the Cr peaks decrease upon annealing. Since the peak heights do not increase, this must be due to a loss of Cr into the PI film.

Fig. 8 shows the AFM picture of the surface of this sample which indicates that the surface is smooth and uniform compared to that of Au in Fig. 3, thus confirming the experimental observations.

III.3. 7 nm Au/PI Prepared at -68 °C

This sample was prepared in the scattering chamber of the Pelletron where the PI and the substrate were kept at -68 °C during gold deposition. By this cooling we wanted to prevent gold atoms from clustering on the surface of the PI and thereby forming islands with many pores along which the penetration of PI to the surface can occur.

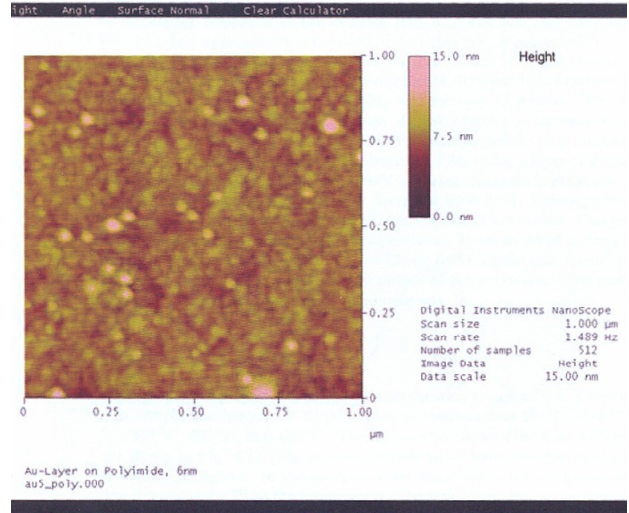


Fig. 6. AFM picture of 5 nm Au/polyimide after annealing at temperatures indicated in Fig. 4

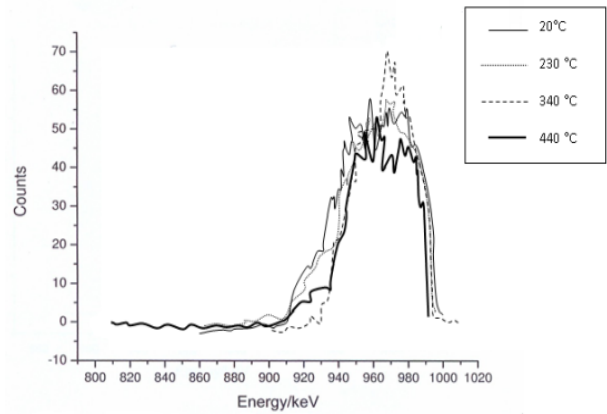


Fig. 7. RBS spectra of 13.5 nm Cr/polyimide annealed at the temperatures indicated in the fig for 30 min. each

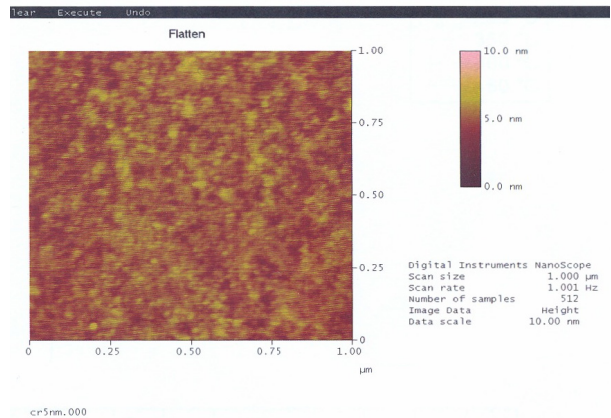


Fig. 8. AFM pictures of 13.5 nm Cr/polyimide after annealing at the temperatures indicated in Fig. 11

This was achieved by means of liquid nitrogen which was passed through tubes attached to the sample holder. One RBS measurement of gold was taken at this temperature and the spectra is shown in Fig. 9. The

sample was then annealed for 30 min. each at the temperatures 20 °C, 300 °C, and 350 °C and RBS spectra taken after each annealing step as shown in Fig. 10. From the RBS spectrum of the 7 nm gold in Fig. 9 and the comparison with simulation we see that the sample is rather uniform with a surface roughness of only 6.7 keV, corresponding to 1.5 nm. In order to anneal the sample at temperatures above room temperature the sample had to be taken out of the scattering chamber and mounted on a different holder. After mounting the sample on the new holder it was not possible to find the old spot on the sample for further RBS analysis. And since the sample is inhomogeneous over the sample diameter of 1 cm the further RBS spectra shown in Fig. 10 look different from the one shown in Fig. 9. As shown in Fig. 10, the film at the new spot is not as homogeneous as the old spot.

There in particular exists no shift of the high energy edge of the spectra towards lower energies which was observed for gold films deposited at room temperature (see Figs. 1 and 4) and which was caused by PI material diffusion to the surface, in this way burying the Au film. The gold film deposited at -68 °C apparently is tight. This is also augmented by comparing the AFM pictures of Fig. 11 and Fig. 6. We see that the surface of the sample deposited at -68 °C is smoother, thus preventing PI from coming to the surface.

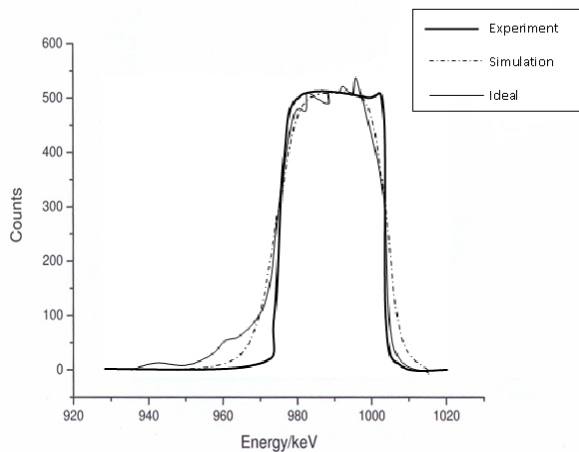


Fig. 9. RBS spectrum and simulation of 7 nm of Au/polyimide

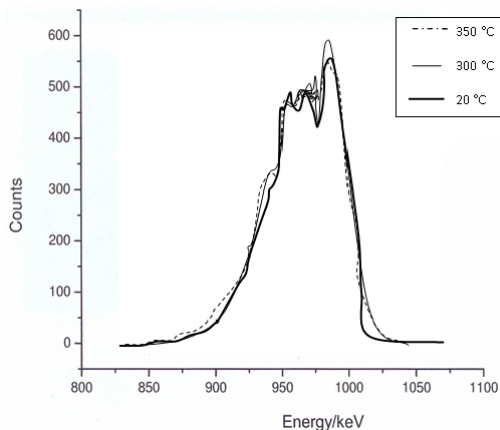


Fig. 10. RBS spectra of 13 nm Au/polyimide after deposition at -68 C and annealed at the indicated temperatures in the figure

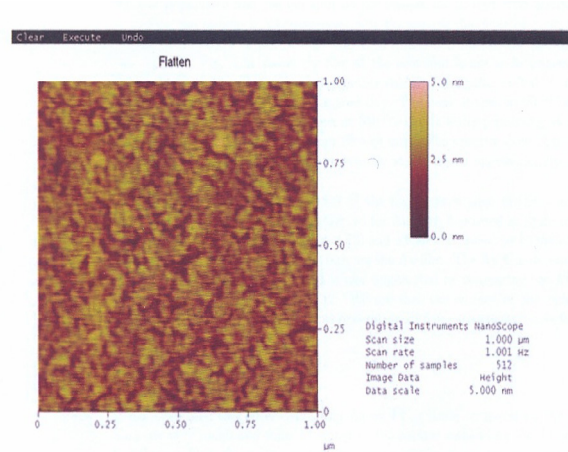


Fig. 11. AFM picture of Au/polyimide at -68 C

IV. Conclusion

It has been seen that after depositing Au on PI at room temperature the Au films are very rough and some PI comes to the surface embedding the Au film. For thinner films there even occurs dissolution and no PI comes to the surface. Since Cr is more reactive than Au, the Cr films are less rough even at room temperature deposition and no PI come to the surface. As such Cr acts as a good buffer between Au and PI for temperatures up to 350 °C. As has been seen when the Au film is deposited at -68 °C the film shows little roughness and is stable up to 350 °C with no PI coming to the surface to cover the film.

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