Thermal stability and adhesion improvement of Ag deposited on Pa-*n* by oxygen plasma treatment

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Parylene-*n* (Pa-*n*) and silver are being studied for ultralarge scale integrated circuits because of their favorable properties. These include low dielectric constant (2.65), negligible water take-up, chemical inertness, low temperature deposition, as well as compatibility with current integrated circuits manufacturing for Pa-*n* and the low resistivity (1.6 $\mu\Omega$ cm), high electromigration resistance for silver. To meet integration requirements, Pa-*n* and Ag are studied to understand specific reliability issues, e.g., diffusion, delamination, or loss of adhesion, compatibility, etc. Initial measurements of silver and dielectric Pa-*n* were done using four-point probe. Thermal stability and texturing of Ag films on Pa-*n* were confirmed using x-ray diffraction analysis. The change associated with resistivity of Ag films on Pa-*n* sample supports the changes observed in x-ray spectra. Rutherford backscattering spectrometry and secondary ion mass spectroscopy analysis show insignificant diffusion of Ag in Pa-*n*. Adhesion analysis of Ag/Pa-*n* and Pa-*n*/Si was done using scratch and tape tests. Oxygen plasma surface treatment of Pa-*n* shows drastic improvement of adhesion between Ag and Pa-*n* without loss of thermal stability of the system. The improvement in adhesion is associated with increased roughness of Pa-*n* surface after plasma treatment. © *2000 American Vacuum Society.* [S0734-211X(00)18906-1]

I. INTRODUCTION

As the features size in modern high density multilevel metallization shrinks, issues such as RC delays, high power consumption, and cross talk noise have to be addressed. One of the solutions for this is to integrate less resistive metal with low dielectric constant materials. Besides having low dielectric constant, the materials must have a good adhesion to silicon and to interconnect materials and thermal stability. Thermal stability is important to device characteristics and reliability. The maximum temperature is not set by dielectric deposition process but by other process requirements such as soldering or annealing. The material is expected to withstand thermal cycling during annealing as well as occasional temperature shocks.

Polyimides[1] have been studied as low dielectric constant material with dielectric constant 3.5–4. Another class of polymers, parylenes, having even lower dielectric constant have been proposed for this work and are evaluated here. For low resistivity interconnect materials, copper is being considered as a good candidate. However, copper diffuses very fast in different materials.[2] Hence, the lower resistivity and relatively noble metal, silver, is considered for our study.

Parylene-*n* (Pa-*n*) and silver are being studied for ultralarge scale integrated circuits because of their favorable properties.[1,2,19,20] These include low dielectric constant (2.65), negligible water take-up, chemical inertness, low temperature deposition,[3] as well as compatibility with current integrated circuit manufacturing and low resistivity (1.6 $\mu\Omega$ cm), high electromigration resistance for silver.

To meet the integration requirements, Pa-*n* and Ag are studied for critical reliability issues. Diffusion of Ag in Pa-*n* was investigated by a series of experiments using Rutherford backscattering spectrometry (RBS), secondary ion mass spectroscopy (SIMS), and x-ray diffraction (XRD) analysis. Variation of resistivity of silver with temperature was measured using four-point probe analysis. Also, adhesion issues of Ag with Pa-*n* were studied using scratch and tape test methods. Oxygen plasma induced surface modification shows drastic improvements in adhesion of Ag with Pa-*n* without sacrificing any electrical or diffusion properties.

II. EXPERIMENT

Parylene-*n* (Pa-*n*) films were deposited on Si substrate by chemical vapor deposition technique. The films were deposited at Paratech Inc. The measured thickness of the films by optical technique was about 1 μm. All the samples selected for the experiment were deposited at one time with the same deposition parameters. Before processing, the above-obtained films were cleaned with acetone, de-ionized water, and dried in dry nitrogen gas.

Silver was deposited on Pa-*n* by electron beam evaporation technique. Operating pressure during evaporation was maintained at 3×10^{-6} Torr. The actual pressure during evaporation was 4.5×10^{-6} Torr. The expected thickness of Ag was 200 nm.

All of the samples were annealed in a tube furnace at different temperatures ranging from 100 to 375 °C. All anneals were done for 30 min under vacuum in a carrousel furnace. The base pressure was 5×10^{-8} Torr and actual pressure during the anneal was approximately 4

$\times 10^{-7}$ Torr. After the anneal was completed the samples were cooled in a load chamber for 15 min before being removed completely from the furnace to avoid sudden decrease in temperature.

X-ray diffraction analysis was performed for structural characterization of Ag films in a Philips X'Pert multipurpose diffractometer (MPD) diffractometer using conventional $\theta/2\theta$ geometry. Cu$K\alpha$ radiation source with an operational voltage of 45 kV and a filament current of 40 mA was used. X-ray diffraction of Pa-n samples in as deposited and annealed conditions was also performed to determine the crystallinity and any phase change.

Conventional RBS measurements with a 3.7 MeV He^{++} ion beam, 7° incident angle, and 172° scattering angle were primarily used for analyzing silver and dielectric interaction and thickness measurements. The beam energy of 3.7 MeV was selected for enhancing the carbon signal[4] from Pa-n.

SIMS was performed for as deposited and annealed samples of Ag/Pa-n system. Camera IMS3f SIMS was used to perform depth profiling. The crater depth was measured on a DekTek profilometer. Ag was removed from the Pa-n using nitric acid. The samples were immersed in 50% nitric acid (50HNO$_3$+50%H$_2$O by volume) for 30 s to remove silver film completely. The silver stripped Pa-n samples were coated with gold to avoid strong charging.

Four-point probe technique was used for sheet resistance measurements. The sheet resistance was measured on both Ag/Pa-n as deposited as well as annealed samples. *In situ* resistivity measurements were done for the Ag/Pa-n sample during thermal annealing. The continuous sheet resistance and temperature measurements were recorded using a computer program. The ramp rate was 20 °C/min and samples were heated in a vacuum. The samples were cooled from 375 to 200 °C in the same furnace and resistivity measurements were again recorded.

Adhesion analysis Ag/Pa-n and Pa-n/Si was done using scratch[5] and tape tests. It consisted of a fixed load applied per test run. The load was increased in 1.1 g increments until the film completely detached from the surface. The stylus made of 20-μm-diam diamond tip was drawn over the surface. The scratches were analyzed using optical and scanning electron microscopes.

Tape test was used as a preliminary adhesion test to screen out poorly adhering films before proceeding with system optimization. The 180° tape test prescribed by the American Society for Testing and Material's designation D3359-95a[6] was performed with Ag/Pa-n films. A pressure sensitive tape (Permecel 99) with minimum adhesional strength of 45 g/mm was applied over a grid of lines manually made by a diamond tip scriber.

To enhance adhesion between Ag and Pa-n, surface modification of Pa-n was performed using an oxygen plasma. Parylene-n was exposed to an oxygen plasma of 50 W plasma for 60 s. The exposed surfaces were analyzed using atomic force microscopy (AFM) and compared to the as deposited sample. Ag is then deposited on Pa-n in a similar way explained above. Some samples were also annealed.
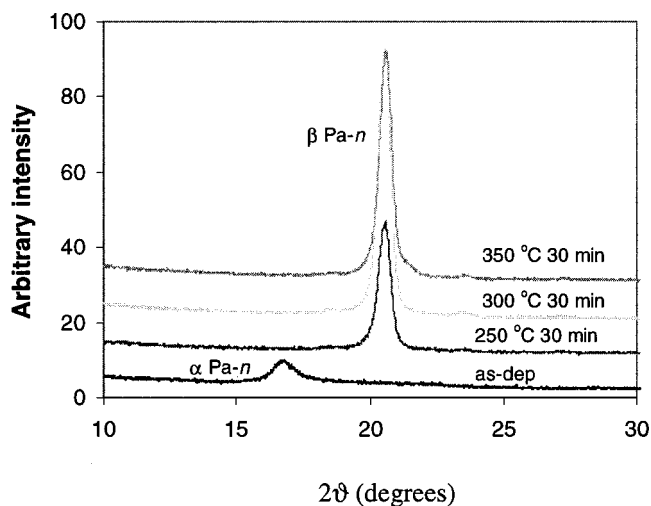

FIG. 1. X-ray diffraction patterns (under $\theta/2\theta$ scan geometry) of Pa-n at different anneal temperatures. The figure clearly shows phase change in Pa-n. The peak corresponding to α Pa-n vanishes at 250 °C and the new peak of β Pa-n is observed.

RBS and four-point probe analysis of the plasma treated surface were performed to check any diffusion or change in electrical properties of silver due to plasma exposure.

III. RESULTS

A. Phase change in Pa-n upon annealing

Figure 1 shows the XRD data of Pa-n film deposited on Si substrate. It was clearly observed that the as deposited sample shows a peak[7] at 2θ equal to 16.6°. This peak corresponds to α phase of Pa-n. The peak completely vanishes at and above 250 °C and a new peak at 20° is formed. This peak corresponds to β phase of Pa-n. This is confirmed with other researchers showing the phase transition of Parylene-n. Literature reveals the phase transformation temperature of Pa-n as 230 °C. The α-Pa-n is a stable phase below 230 °C and completely transformed to β-Pa-n, which is irreversible
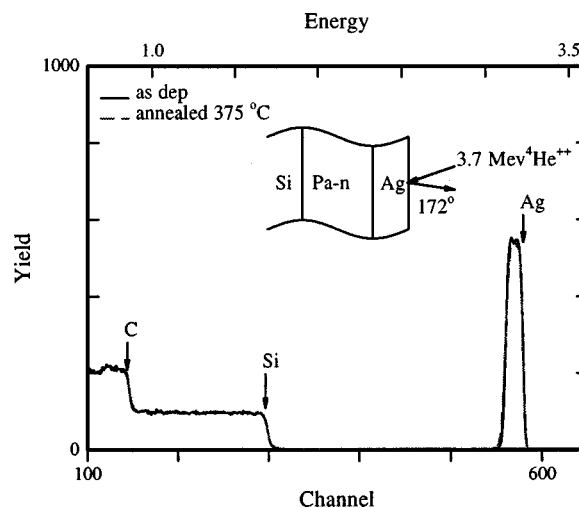

FIG. 2. Typical RBS spectra of as deposited and 375 °C annealed Ag/Pa-n films. Both spectra show no diffusion of Ag when deposited on Pa-n.
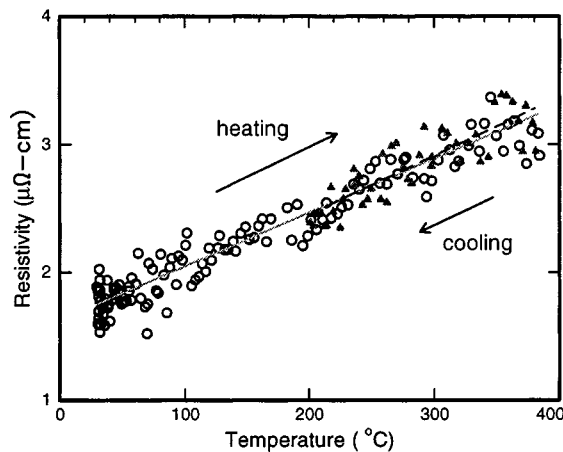
FIG. 3. *In situ* analysis of resistivity variation of Ag on Pa-*n* with temperature by four-point probe measurements. The resistivity follows linear relationship with temperature. (○-heating, △-cooling, — represents linear fit while heating and - - - represents linear fit while cooling down).
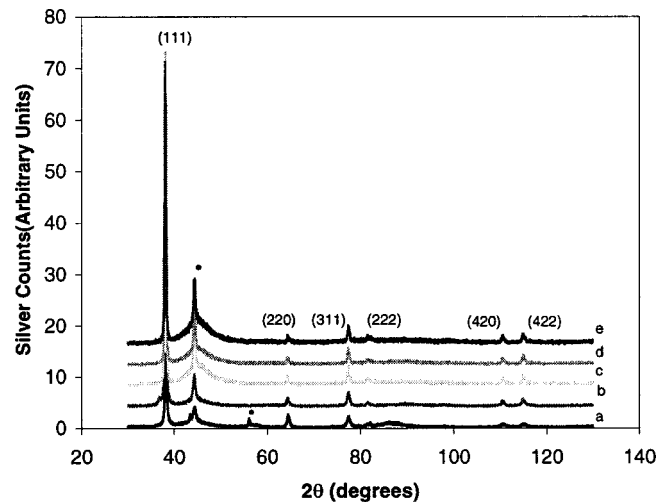

FIG. 4. XRD diffraction patterns (under $\theta/2\theta$ scan geometry) of Ag/Pa-*n* at different anneal temperatures.

and stable after cooling down to room temperature.[8] Increase in intensity of the β-Pa-*n* indicates an increase in the crystallinity of the Pa-*n* as it is annealed at higher temperatures.

B. Compositional changes of Ag on Pa-*n* upon annealing

The silver film thickness obtained from RBS was approximately 180 nm and for Pa-*n* it was 0.8 μm. Experiments showed no significant changes in Ag films upon annealing. Figure 2 shows a comparison of the as deposited and annealed Ag films on Pa-*n*. Energy of 3.7 MeV was used for RBS analysis and corresponds to the resonance energy for nitrogen.[8] It also enhances carbon and oxygen signals in the spectra and hence was used to clearly distinguish carbon signal from Pa-*n*. Literature shows that silver diffuses in Pa-*n* above 350 °C for 30 min anneals. Our data suggest no RBS detectable diffusion of Ag in Pa-*n* even at 375 °C and 1 h anneals.

C. Sheet resistance variation upon annealing

In situ four-point probe measurements of Ag on Pa-*n* were performed as explained in the previous section. The obtained sheet resistance, values of Ag were converted to resistivity by using thickness values obtained from RBS. The plot of resistivity as a function of temperature is shown in Fig. 3. Also, ramp up and cool down data are plotted in the same graph. As both cool down and ramp up observations follow the same line, it can be said that there is no drastic change in the silver film deposited on the Pa-*n*. This analysis shows resistivity changes linearly with temperature.

TABLE I. Resistivity of Ag/Pa-*n* with annealing temperature.

Sample	As deposited	100 °C	250 °C	300 °C	350 °C
R $\mu\Omega$ cm	2.73	2.55	1.95	1.87	3.48

The *ex situ* analysis of resistivity of Ag on Pa-*n* is shown in Table I. The variation of resistivity can be best explained with XRD analysis mentioned below. Figure 4 shows x-ray diffraction pattern of Ag on Pa-*n*. Ag film shows prominent (111) peak. The intensity of (111) peak increases up to 300 °C and then suddenly decreases for 350 °C. X-ray diffraction does not reveal any phase formation of Ag with Pa-*n* even at elevated temperatures. Annealing above 400 °C decomposes Pa-*n* films.

D. Diffusion analysis using SIMS

SIMS analysis was performed on Ag films on Pa-*n* to confirm any diffusion of silver in Pa-*n* at high temperatures which may be undetected by RBS analysis due to resolution and sensitivity limitations. Figure 5 shows a comparison of silver counts normalized to carbon counts for bare Pa-*n*, as deposited Ag, and annealed silver at 375 °C as a function of apparent depth. The term apparent depth was used as it was derived from actual depth measured with a profilometer. From the graph it can be seen that both as deposited and
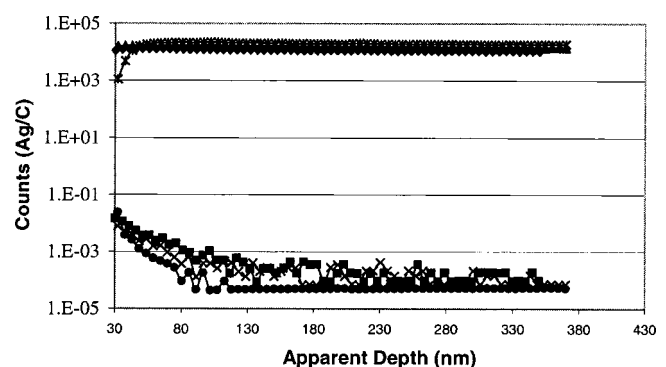

FIG. 5. Comparison of SIMS profiles of silver counts for bare Pa-*n*, as deposited Ag/Pa-*n*, and 375 °C annealed Ag/Pa-*n*. The linear portion of spectrum was used to determine the diffusion coefficient of the annealed silver. The diffusion is barely above the background. (♦ C as deposited, ■ Ag/C as deposited, ▲ C 375 °C, × Ag/C 375 °C,* C bare, ● Ag/C bare.)

TABLE II. Scratch test results of failure load in grams.

Sample	As-deposited	250 °C	300 °C	350 °C
Pa-n/Si	8.0	6.9	5.5	4.5
Ag/Pa-n/Si	4.4	4.4	5.5	5.5

TABLE III. Tape test results for Ag/Pa-n. If more than 25% of total film was removed, then the sample considered to be failed.

Sample	Tape test criteria	Remarks
As/Pa-n as deposited	Fail	90% silver film removed
Ag/Pa-n 250 °C	Pass	20% silver film removed
Ag/Pa-n 300 °C	Pass	10% silver film removed
Ag/Pa-n 350 °C	Pass	<2% silver film removed
Ag/Pa-n 375 °C	Pass	<2% silver film removed

annealed curves follow each other indicating no silver penetration in parylene even after annealing at 375 °C for 30 min. Silver counts in both cases are more than bare Pa-n as expected.

E. Adhesion analysis

Table II shows total load in grams required to remove film of Pa-n from the Si substrate completely after performing the scratch test. It was observed that load decreases with increasing annealing temperature suggesting deterioration of adhesion of Pa-n with Si substrate. Figure 6 shows optical microscope images of the scratch test. Table II also shows that the load required to remove Ag film completely from Pa-n increases with increasing annealing temperature. This indicates stronger adherence of Ag with Pa-n at elevated temperatures.

To support the results from the scratch test, results from the adhesion tape test were examined. If more than 25% of the total tested film was removed, then the sample was considered to be ''Failed'' in the adhesion test. Table III shows the results of the tape test for different conditions. The as deposited Ag film on Pa-n shows the removal of more than 90% of the film, indicating very poor adhesion. The annealing above 250 °C improves the test results significantly.

Though annealing increases the adhesion of silver to parylene to some extent, surface modification of parylene even shows better results. AFM was used to compare the as deposited and plasma treated parylene surfaces (Fig. 7) at an
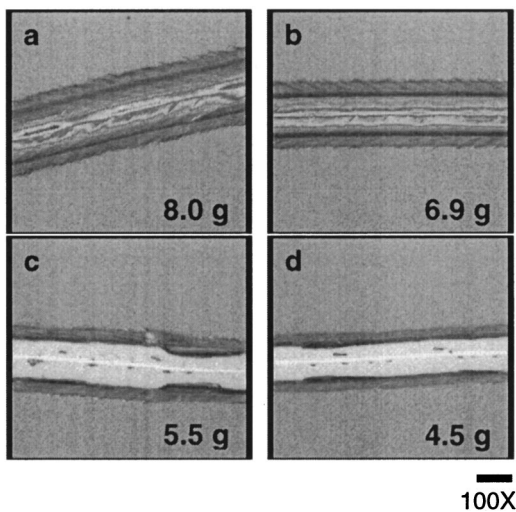
atomic scale. Oxygen plasma induces damage to the parylene surface and hence increases its roughness. The rough films are believed to increase mechanical interlocking between top silver and bottom parylene film, thereby increasing the adhesion significantly. Tape test after surface modification shows that adhesion between Ag and Pa-n is even stronger than Pa-n and Si substrate. Four-point probe and RBS analysis performed on the above samples show no drastic difference as compared to untreated samples.

IV. DISCUSSION

Results of the above experiments indicate very little tendency of silver to diffuse in parylene. Secondary ion mass spectroscopy reveals an insignificant amount of silver in parylene at 375 °C. It was assumed here that diffusion takes place according to Fick's law.[9] The plot of natural log of concentration of silver against square of depth was used to find the diffusion coefficient[9] of silver. The slope of the graph was equated to $1/4Dt$, where D is diffusion coefficient and t is time in seconds. For silver sample annealed at 375 °C for 30 min, calculated diffusion coefficient was $1.47 \times 10^{-14} \pm 3\%$ cm^2/s. This calculated diffusion coefficient is smaller than previously recorded values.[10] The value is also approximately equal to the as deposited silver on parylene, suggesting that silver concentration in the parylene remains constant during annealing. This insignificant silver diffusion in parylene can be explained as follows.

During annealing, Pa-n changes from α-Pa-n which has monoclinic crystal structure to β-Pa-n which is trigonal.[8] During this transformation, crystallinity of parylene increases. This was shown by XRD in Fig. 1. Typical parylene is only 57% crystalline and the remainder is amorphous. Though its crystallinity increases with annealing it never
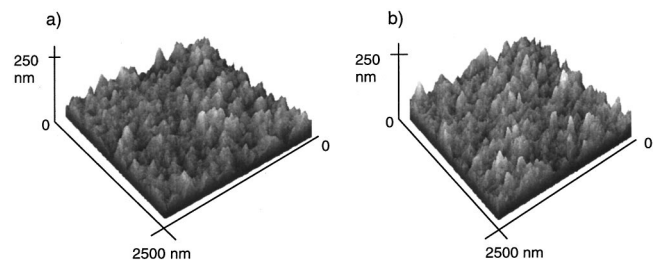

FIG. 6. Scratch test analysis of Pa-n on Si with different annealing temperatures. (a) As deposited, (b) 250 °C, (c) 300 °C, and (d) 350 °C. All anneals were performed in vacuum for 30 min. The load required to remove the film completely from the silicon substrate is denoted.

FIG. 7. Atomic scale pictures of Pa-n surface obtained by AFM. (a) Untreated, as deposited Pa-n on Si, and (b) oxygen plasma treated Pa-n. More peaks and valleys were seen indicating a rough Pa-n surface after plasma treatment.

reaches 100% crystallization. The amorphous region in parylene may be present between the crystalline structure. The whole surface can be considered as long crystalline chains linked together with amorphous regions forming a closed structure.[11] This closed structure is believed to prohibit diffusion of silver in Pa-*n*. Some researchers have shown a web-like structure[12] at the interface of Pa-*n* and Cu, increasing Cu diffusion drastically. No such web structure was observed at the Pa-*n* and Ag interface when examined at high magnification using scanning electron microscopy. An experiment was conducted to examine the effect of phase change of Pa-*n* on silver diffusion. Pa-*n* was preheated to 250 °C for 30 min to allow complete phase transformation from α phase to β phase and then cooled down. The α to β transformation is irreversible. β Pa-*n* is more crystalline as compared to α Pa-*n* and hence it was more open. Ag is deposited at room temperature on the pre-annealed sample and then the system is again annealed at 375 °C for 30 min in vacuum. SIMS analysis on annealed sample does not reveal any diffusion of silver in Pa-*n*. This shows that phase change of Pa-*n* does enhance diffusion of silver.

The atomic size is another effective factor for silver atom. Diffusion is recorded for copper and aluminum before in Pa-*n*.[17] Copper and aluminum atom sizes[13] are 0.135 and 0.126 nm, respectively. These are smaller as compared to silver atom which has a covalent radius of 0.152 nm. Thus it requires more space to pass through Pa-*n* structure underneath it. Silver has a melting point of 962 °C which is not enough to thermally excite silver atoms at 375 °C to go under diffusion.

Thermal stability of silver is explained using the four-point probe technique. It was observed during *in situ* resistivity variation with temperature that the cool down curve exactly follows the ramp up curve. This rules out any formation of voids in silver film while annealing. This suggests that silver film maintained its continuity up to 375 °C during annealing. Also, the mechanical and thermal strains produced during deposition and annealing are not significant enough to cause any discontinuity in silver or parylene films.

Adhesion is very important in determining durability of thin film devices.[14] Here qualitative study of adhesion of Pa-*n* with silicon substrate as well as top silver layer was presented. Si wafers were cleaned in HF solution before depositing Pa-*n* on it by vapor deposition at Paratech Inc. The adhesion was examined using the scratch test. It was observed that adhesion between Pa-*n* and Si substrate deteriorates with annealing. Pa-*n* is a chemically inert polymer and it does not form any chemical bond with Si substrate.[15] This indicates inherent adhesion of Pa-*n* with Si is poor. In the absence of any adhesion promoter and surface treatment, two smooth surfaces result in weak adhesion. The possibility of small silicon dioxide at the interface between Pa-*n* and Si and defects may cause a reduction in adhesion.[18]

Formation of chemical bonds is an important way to achieve interfacial adhesion.[14] For silver and the Pa-*n* system there does not exist any chemical interactions, such as second phase formation or intermixing with each other, re-

sulting in weak adhesion. This was confirmed by x-ray diffraction and SIMS results. Small dipole–dipole interaction between the two, though cannot be neglected. However, the tape test shows improved adhesion between silver and parylene with annealing. The reason for this is not fully understood at this time. Future study will address this behavior specifically.

Although annealing increases the adhesion, it is not enough for reliable device operation. One way to improve the adhesion is by surface treatment of Pa-*n*. Oxygen plasma was used to treat the Pa-*n* surface. Plasma treated Pa-*n* showed evidence of increased roughness.[16] Figure 7 shows AFM pictures of untreated and oxygen plasma treated Pa-*n* surfaces. The plasma treated samples were analyzed using the tape test for adhesion. It was observed that adhesion between Ag and Pa-*n* is stronger than even Pa-*n* and Si substrate. The tape test shows complete removal of Ag/Pa-*n* together from Si substrate. Due to increased roughness, contact area between Ag and Pa-*n* was increased, improving adhesion tremendously. Care should be taken while doing plasma treatment, as excess power or long time exposure can etch Pa-*n* completely. Formation of single and double bonds between carbon and oxygen[11] during plasma treatment may have helped increase adhesion between Ag and Pa-*n*.

V. CONCLUSIONS

The thermal stability of Pa-*n* as interlayer low dielectric material and silver as low resistivity metal was studied. No interaction of phase formation between Ag and Pa-*n* was observed. Resistivity analysis by four-point probe shows the structure to be electrically stable even at high annealing temperatures ($\sim$375 °C). Phase change of Pa-*n* while annealing does not affect diffusion properties of Ag in Pa-*n*. SIMS gave a diffusion coefficient of $1.47\times10^{-14}\pm3\%$ cm^2/s for as deposited as well as annealed samples, indicating negligible diffusion of silver in Pa-*n*. Although adhesion between Ag and Pa-*n* is poor, it is shown that drastic improvement can be obtained by surface treatment of Pa-*n* with oxygen plasma without sacrificing thermal and electrical stability of the system.

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