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<td>Gan, Zhenghao; Chen, Zhong; Mhaisalkar, Subodh Gautam; Damayanti, M.; Chen, Zhe; Prasad, K.; Zhang, Sam; Jiang, Ning</td>
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Effect of electron beam treatment on adhesion of Ta/polymeric low-\(k\) interface

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Reliability of the Cu/low-\(k\) structure is a serious concern since the metal/dielectric interface is generally weak. The adhesion of the Ta/polyarylene ether interfaces with and without electron beam (EB) treatment was investigated by four-point bending test, x-ray photoelectron spectroscopy, and density functional theory. Higher adhesion energy \((G_c)\) was achieved with low-dose EB treatment, attributed to the strong Ta-arene interaction. However, high-dose EB breaks the aromatic rings partially, resulting in fewer available sites for Ta-arene bonding, leading to lower adhesion. It is suggested that the amount of carbon atoms involved in bonding with the metal is the key to improve the Ta/polymer adhesion. © 2006 American Institute of Physics. [DOI: 10.1063/1.2212533]

Polymeric low-\(k\) dielectrics have been introduced in the Cu damascene structures as a result of increasing demand on integrated circuit (IC) device density and performance.\textsuperscript{1,2} Porous polyarylene ether (PAE) has been proposed as one of the candidates because of its low dielectric constant (2.65–3.0) and high thermal stability (>425 °C).\textsuperscript{2,3} A metallic barrier layer such as Ta is always employed to block Cu diffusion into the dielectrics.\textsuperscript{4} Reliability of the Cu/low-\(k\) structure is a serious concern since the metal/dielectric interface is generally weak. Electron beam (EB) curing can effectively make the cage-like bonds of porous organosilicate glass (OSG) transfer to network bonds, thus improving adhesion property.\textsuperscript{5} However, other work found that EB treatments on OSG did not improve interfacial adhesion significantly (<10%).\textsuperscript{5} Previous study showed that EB treatment could reduce line-to-line leakage current in Cu/Ta/PAE interconnect comb structures, attributed to the reduced oxygen content at the Ta/PAE interface.\textsuperscript{7} In this letter, we demonstrate that EB treatment with controlled dose could improve adhesion of the Ta/PAE interface. The underlying mechanism is revealed by x-ray photoelectron spectroscopy (XPS) analysis and density-functional theory (DFT) calculation.

The chemical structure of PAE precursor is shown as the inset in Fig. 1.\textsuperscript{2} A 300-nm-thick PAE film was deposited on an 8-in.-diameter \(p\)-type Si(100) wafer using spin-on technique. A 25-nm-thick Ta layer was then deposited immediately by physical vapor deposition. The film thickness was confirmed by transmission electron microscopy (TEM) examination. Two other wafers with PAE film were exposed under EB in a vacuum chamber by employing an EB scan system prior to Ta deposition. The doses for the EB exposure were 20 \(\mu\)C/cm\(^2\) (low dose) and 40 \(\mu\)C/cm\(^2\) (high dose), respectively, with the same energy (50 keV). XPS measurements were carried out to investigate interface chemistry and depth profile in a Kratos AXIS spectrometer\textsuperscript{8} (UK) with the monochromatic Al \(K\alpha\) x-ray radiation at 1486.71 eV and base vacuum of \(\sim 10^{-9}\) Torr. The adhesion strength, in terms of critical energy release rate \((G_c)\) of the Ta/PAE interface, was quantified by four-point bending (4PB) technique.\textsuperscript{9} For each case, ten samples were tested.

Figure 1 compares the XPS depth profile of Ta/PAE low-\(k\) interfaces. Small amount of Ta atoms may diffuse into the PAE film, mainly attributed to the porous characteristic of

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FIG. 1. XPS depth profile of Ta/PAE low-\(k\) interface: (a) without, (b) with EB treatment (20 \(\mu\)C/cm\(^2\)), and (c) with EB treatment (40 \(\mu\)C/cm\(^2\)). The inset shows the chemical structure of PAE precursor, where Ar and Ph are short for aryl and phenyl, respectively.
TABLE I. Comparison between experiments and DFT simulation.

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<th>DFT simulation</th>
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<tr>
<td></td>
<td>Gc (J/m²)</td>
<td>Binding energy</td>
</tr>
<tr>
<td>x (TaC₃ at</td>
<td></td>
<td>Gc (J/m²)</td>
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<td>interface)</td>
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<tr>
<td>without EB</td>
<td>-1.8</td>
<td>5.9±1.1</td>
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<tr>
<td>Low-dose EB</td>
<td>-2.3</td>
<td>8.1±0.5</td>
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<tr>
<td>High-dose EB</td>
<td>-0.2</td>
<td>4.0±0.6</td>
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PAE. Similar Ta diffusion was observed at the Ta/porous α-
SiC:H interface. It is clear that no inherent oxygen was
detected in the bulk of the PAE film, mainly due to its low
content less than the sensitivity of the XPS equipment. For
the case without EB treatment [Fig. 1(a)], about 20% of the
atoms located in the Ta/PAE interface are oxygen. This
interfacial oxygen may be a result of oxygen/moisture absorp-
tion during process transfer from PAE deposition to physical
vapor deposition (PVD) barrier deposition. Similar XPS
spectra of PAE and the incorporation of oxygen were re-
ported earlier.

On the other hand, the O species were hardly detected at the Ta/PAE
interface with EB treatments [Figs. 1(b) and 1(c)]. It is con-
ceivable that high energy electrons would break the weakly
bonded oxygen.

The Gc values of Ta/PAE interfaces obtained by 4PB in
the current study were 5.9±1.1, 8.1±0.5, and 4.0±0.6 J/m²
with EB doses of 0, 20, and 40 μC/cm², respectively (Table
I). The error of the Gc value is caused by the variation in the
critical flaw among test specimens due to the porous nature
of the Ta/PAE interface. It is noted that the Ta layer was thin
(25 nm); therefore, the plastic deformation effect should be
negligible during the 4PB measurement. The measured Gc
values were also comparable to those of other Ta/low-k
interfaces. It is interesting that the adhesion energy in-
creased about 37% when EB dose was 20 μC/cm², which
could be attributed to the active PAE surface induced by the
EB, thus improving the Ta-PAE bonding. However, with the
higher-dose EB treatment, Gc value reduced by about one-
third compared to the pristine case. One possible explanation
may be the damage caused by the EB treatment. However,
the higher EB dose of 40 μC/cm² in our study is much
lower than that of immersing system in a conventional EB
curing process (~500 μC/cm²), where no damage was ob-
served under in-line field emission scanning electron micros-
copy.

Figure 2 gives the comparison of spectra deconvolution
of C 1s for all cases at around 40 nm depth. For pristine
interface [Fig. 2(a)], the spectrum could be deconvoluted into
to three components, corresponding to C-Ta (at
283.2 eV), C-C (at 285 eV), and C-O bonds (at 287 eV), re-
spectively. With EB treatments, either low dose [Fig. 2(b)]
or high dose [Fig. 2(c)], the C-O bond is not detectable
because the absorbed O species were removed by EB. In
addition, the relative amount of C-Ta bonds increased with
lower-dose EB treatment [Fig. 2(b)], whereas they decreased
substantially with higher-dose EB treatment [Fig. 2(c)]. If we
consider the TaC₃ compound formed at the interface, values
of x are around 1.8, 2.3, and 0.2 for pristine, low-dose, and
high-dose EB treatments, respectively (Table I). Several
references have mentioned that the formation of C-Ta bonds at
the interface can improve the adhesion. Therefore fewer
C-Ta bonds may be the main reason leading to the lower
adhesion energy of the specimens with higher-dose EB treat-
ment.

The Ta/PAE interfacial interaction involves the charge
transfer complexes between the metal and the entire aromatic
π system, previously proposed for Cr on pyromellitic
dianhydride-oxide-dianiline (PMDA-ODA). With the lower
dose of EB treatment, the aromatic complexes at the PAE
surface are more active and more Ta–C bonds will form,
leading to a stronger interface. However, if a high dosage is
imposed, the C–C or C–H bonds may be partially broken,
resulting in fewer available sites for Ta-arene bonding. Thus,
with the higher-dose EB treatments, fewer carbon atoms will
be bonded to Ta atoms as demonstrated by XPS (Fig. 2),
leading to lower adhesion.

Here we present an energetic analysis from first prin-
ciples calculation for the binding energy of a single Ta to a
benzene complex [Fig. 3(c)] and that to a single C atom in
the aromatic ring [Fig. 3(b)]. Following the method to calcu-
late the cohesive energy, the binding energy is derived by
subtracting the energies of an isolated Ta atom and an iso-
lated benzene molecule [Fig. 3(a)] from the total energy of
the configuration shown in Fig. 3(b) and 3(c). The calcula-
tion using isolated benzene molecule and Ta(C6H6), in one
way, is to save computational time but, in the other way,
could get a preliminary insight on the Ta-arene interaction.

Similar simplification was adopted by others to study the
metal-arene compounds. The calculations were performed
using DFT-based CASTEP. The exchange-correlation energy
is described by GGA-PBE. The Brillouin zone is sampled with
a Monkhorst-Pack k-point grid.
shown in Fig. 3 are placed in a $15 \times 15 \times 15 \, \text{Å}^3$ supercell. A $\{1 \times 1 \times 2\}$ k-point mesh was used with plane-wave cutoff at 260 eV. After relaxing the structure of Fig. 3(c), the Ta atom is exactly located above the center of the aromatic ring with Ta–C bond length of 2.16 Å, which agrees very well with the reported value of 2.205 Å in a TaC crystal. The calculated binding energy for a single Ta-arene complex is $-3.8$ eV [Fig. 3(c)], indicating that the system will be more stable after Ta binding to the benzene. It is interesting to estimate the macroscopic adhesion energy based on the calculated binding energy as follows. In Fig. 3(c), the C–C and C–H bond lengths are 1.39 and 1.09 Å, respectively. The area of a single arene is about $6.44 \times 10^{-20} \, \text{m}^2$, giving an adhesion energy value of $5.9 \times 10^{-19} \, \text{eV/m}^2$, i.e., $9.4 \, \text{J/m}^2$. This value is $-16\%$ higher than the measured $G_c$ of the low-dose EB treated Ta/PAE interface $(8.1 \, \text{J/m}^2)$ and should be considered as an upper bound of $G_c$ since the PAE is porous and its surface may not be fully covered by the arene repeating units. On the other hand, the calculated binding energy for Ta interacting with single C atom in the aromatic ring [Fig. 3(b)] is $-2.6$ eV (Table I). The corresponding estimated $G_c$ is $6.4 \, \text{J/m}^2$, which is weaker than the Ta-arene interaction in Fig. 3(c).

Additional insight can be gleaned from the calculated density of states (DOS) of the different configurations (Fig. 3). The Fermi levels are set to 0 eV. It is seen that there is a band gap between 0 and 5 eV for the isolated benzene [Fig. 3(a)], which disappears after Ta atom is bonded to the benzene [Figs. 3(b) and 3(c)]. All the energy peaks in Ta-benzene curves [Figs. 3(b) and 3(c)] shift downwards in energy relative to the corresponding peak in the free benzene curve. However, the amount shifted is larger when the Ta atom is on top of the arene [Fig. 3(c)], indicating that more C atoms are involved in bonding with the metal, corresponding to the lower-dose treated Ta/PAE interface. This is consistent with the larger x value of TaC$_x$ compound by XPS, the higher microscopic binding energy by DFT calculation, and the higher macroscopic $G_c$ by 4PB (Table I).

In summary, we demonstrated that different dosage of EB treatment could either improve or deteriorate adhesion of the Ta/PAE interface. The $G_c$ values of Ta/PAE interfaces obtained by four-point bending are 5.9±1.1, 8.1±0.5, and 4.0±0.6 J/m$^2$ with EB doses of 0, 20, and 40 $\mu$C/cm$^2$, respectively. Both DFT calculation and XPS analysis indicated that the amount of carbon atoms involved in bonding with the metal is the key to improve the Ta/polymer interfacial adhesion.