Title
Copper CMP Modeling: Millisecond Scale Adsorption Kinetics of BTA in Glycine-Containing Solutions at pH 4

Permalink
https://escholarship.org/uc/item/0pn4r425

Authors
Choi, Seungchoun
Tripathi, Shantanu
Dornfeld, David
et al.

Publication Date
2010-10-28

Peer reviewed
Copper CMP Modeling: Millisecond Scale Adsorption Kinetics of BTA in Glycine-Containing Solutions at pH 4

Seungchoun Choi, a Shantanu Tripathi, a David A. Dornfeld, a and Fiona M. Doyle b,c,d

a Department of Mechanical Engineering and b Department of Materials Science and Engineering, University of California, Berkeley, Berkeley, California 94720, USA

Millisecond scale benzo triazole (BTA) adsorption kinetics in acidic aqueous solution containing 0.01 M glycine and 0.01 M BTA have been investigated. Chronoamperometry was used to measure current densities on the surface of a micro-copper electrode in pH 4 aqueous solutions containing 0.01 M glycine with or without 0.01 M BTA. In the presence of BTA the current density decreased as the inverse of the square root of time for a few seconds due to adsorption of BTA. At potentials above 0.4 V saturated calomel electrode the current leveled off after a second or so due to the formation of a CuI/BTA monolayer on the copper surface. Based on these data a governing equation was constructed and solved to determine the initial kinetics of BTA adsorption. Analysis shows that material removal during copper chemical mechanical planarization (CMP) in this slurty chemistry occurs mostly by direct dissolution of copper species into the aqueous solution rather than mechanical removal of oxidized or pure copper species and that each interaction between a pad asperity and a given site on the copper removes only a small fraction of the CuI/BTA species present at that site.

© 2010 The Electrochemical Society. [DOI: 10.1149/1.3499217] All rights reserved.
should be over in less than a millisecond, since the maximum behavior is very different in the absence of BTA. The current density varies as the inverse of the square root of time. The Cottrell-type decay behavior in the presence of BTA suggests this. EIS data for these solutions containing both 0.01 M glycine and 0.01 M BTA. At first sight this suggests a Cottrell-type decay behavior in the presence of BTA (Fig. 1), with current densities determined by diffusion of BTA to the copper surface. However, given the fact that the current is strongly affected by the fraction of sites occupied by BTA, as discussed below, there is no compelling evidence for diffusion control. At lower potentials (< ~0.2 V) in Fig. 1, the anodic currents eventually became lower in magnitude than the cathodic current due to hydrogen evolution, causing the net current to become cathodic.

Several researchers have examined the interaction of BTA with copper substrates, both adsorption and the formation of polymeric CuBTA films, albeit over much longer time scales than those studied here. A 1:1 stoichiometric association of Cu with BTA in adsorbed layers indicates the formation of a Cu(I) species. BTA has been reported to adsorb on copper at low pH, lower potentials, and low adsorption densities, while polymerized Cu(I)BTA multilayers appear at high pH, higher potentials, and higher adsorption densities. Adsorption has been reported on both oxide-free copper surfaces and Cu2O. Youda et al. and Tromans presented pH diagrams that show Cu(I)BTA predominating at pH < 4 aqueous solutions at oxidizing potentials, but these are equilibrium diagrams and may not reflect the dynamic condition during active polishing of copper, where any adsorbed BTA is regularly disturbed by pad asperities and copper is continuously oxidized. Nevertheless, it is evident that the copper on the surface is oxidized to form a protective layer of BTA.

At some of the higher potentials in Fig. 1 (> 0.4 V), the current densities leveled off after a few seconds. This suggests that there is no more adsorption of BTA or any subsequent adsorption of BTA provides no further passivity. Although at first sight the transition could be associated with a change in behavior for either a monolayer or a Cu(I)BTA multilayer, it is unlikely that a multilayer could have developed to the point of establishing a limiting current in just a few seconds. Furthermore, since the formation of a monolayer involves diffusion of BTA through the boundary layer at the copper–solution interface whereas the formation of a Cu(I)BTA multilayer involves transport of species through layers that had already formed, which is much slower than boundary layer diffusion, one would expect a change in gradient when monolayer formation changed to multilayer formation. As discussed above, the change in gradient in Fig. 1 below 1 ms has been correlated with the cessation of capacitive charging, and there are no further changes in gradient until those seen at a few seconds. Hence, this point can reasonably be assumed to correspond to complete occupancy by BTA of the available anodic sites on the copper surface, i.e., the formation of a protective monolayer on the copper surface. The time at which the monolayer first forms is designated as \( t_m \). Any subsequent uptake of BTA is assumed to correspond to the precipitation of polymerized multilayers by the interaction of copper ions that had previously dissolved into the aqueous solution with BTA species diffusing to the surface region from the bulk. If this is the case, the removal of the precipitated layers would not contribute to the material removal during copper CMP, regardless of the amount of copper within them, because this copper will have already been accounted for as direct dissolution from the copper surface.

**Quasisteady-State Assumption**

As noted above, for computational efficiency Tripathi et al. postulated a quasisteady state during copper CMP such that on average the amount of protective film removed at each asperity–copper interaction is equal to the amount of film that reforms before the next interaction. In principle, the estimation could have considered successive abrasive particle–copper interactions rather than asperity–copper interactions. However, the interval between sequential abrasive particle–copper interactions under an asperity was estimated at less than 10 \( \mu s \), which is 2 or 3 orders of magnitude smaller than the interval between asperity–copper interactions (1–10 ms). Hence the electrochemical changes on copper between sequential abrasive contacts under the same asperity would be minor compared to the electrochemical changes occurring between two asperity contacts. Indeed, assuming that the abrasive particles are relatively uniformly distributed under each asperity, they can be considered part of the asperity itself and most likely provide the “chemical tooth” that preferentially interacts with Cu–BTA complexes. Therefore, only the interval between two consecutive asperity–copper interactions was considered in the concept of a quasisteady state.

The oxidation rates shown in Fig. 1 decrease from about 0.05 A/cm² immediately after capacitive charging has ceased to about 0.003 A/cm² or less at \( t_m \) equivalent to material removal rates declining from about 1100 to 66 nm/min or less (assuming that...
Cu(I) is formed. For copper CMP in slurries containing BTA and glycine, typical material removal rates are 130–600 nm/min.5 Since these rates lie between the rates corresponding to the extreme currents seen in Fig. 1, it appears that during most copper CMP operations there is less than a monolayer of BTA on the copper.

Figure 3 schematically illustrates the establishment of the quasi-steady state when the copper surface is partially covered by Cu(I)BTA between pad asperity–copper interactions. The upper curve shows the fraction of the copper surface sites occupied by Cu(I)BTA at any time. It is assumed that an asperity moving across the surface will remove a constant fraction of all the Cu(I)BTA present. It is implicit in this assumption that the mechanism for removing Cu(I)BTA species is preferential adsorption onto abrasive particles held under the asperity and that the abrasive particles themselves will already have some sites occupied by Cu(I)BTA because of either previous interactions with copper or through having adsorbed dissolved copper and BTA in the slurry. Figure 3 was constructed assuming (arbitrarily, to illustrate the principle involved) that 20% of the Cu(I)BTA species present on the copper surface at any time are removed by a given interaction with a pad asperity regardless of the absolute concentration of the species on the surface (shown as the dashed line). It is assumed that when abrasion starts there is a monolayer of Cu(I)BTA present (at least a monolayer is reasonable, given that the time taken to move a copper-covered wafer into position above a polishing pad exceeds the values for \( t_m \) seen in Fig. 1) and that the fraction of surface sites occupied by Cu(I)BTA after the first interaction corresponds to the state at \( t_m \) (indicated by the downward arrow and horizontal dashed line). More Cu(I)BTA forms on the copper surface before the next asperity–copper interaction (indicated by the upward arrow) but the time, \( \tau \), until the next interaction is not long enough to reform a monolayer. Accordingly, the next abrasion [again assuming that it removes 20% of all Cu(I)BTA on the surface] will further reduce the coverage of the surface by Cu(I)BTA beyond that achieved in the first interaction to one corresponding to a different state at \( t_m \). This process is repeated \( n \) times until a quasisteady state is reached where exactly as much Cu(I)BTA is removed during an asperity–copper interaction as is reformed in the interval before the next interaction, \( \tau \) (at \( t_m \)). Note that the duration of the asperity–copper interaction is very short compared to the interval between asperity–copper contacts and no significant electrochemical reaction occurs during the interaction itself. (The electrochemical state at the beginning of a single interaction is almost the same as that at the end of the interaction.) Hence the asperity–copper interactions are denoted by vertical lines, while the reformation of Cu(I)BTA is relatively gradual and is shown as diagonal lines.

Regardless of the initial condition, because the reduction of coverage upon abrasion and the gain in the coverage during \( \tau \) is always equal once the quasisteady state has been reached, the vertical and diagonal arrows in Fig. 3 cycle inside of the dashed circle [i.e., the fractional coverage immediately after the \( n \)th abrasion is the same as that immediately after the \((n+1)\)th abrasion]. This introduces the time parameter \( t_0 \), defined by

\[
\tau^* = t_{n+1}^* = t_{n+2}^* = \cdots = t_0
\]  

Faraday’s law can be invoked to express the balance between the amount of Cu(I)BTA formed at the surface and the amount removed

\[
\int_{t_0}^{t_{n+1}} \rho \int_{\Delta t} \text{d}M \text{d}t = \frac{\Delta q(t_0 + \tau)}{t_0}
\]  

where \( \Delta q(t) \) is the charge density of the oxidized copper within the Cu(I)BTA removed from the copper surface during an abrasion event at time \( t \), \( \rho \) is the current density that contributes to the formation of Cu(I)BTA on the surface at time \( t \), and \( \tau \) is the interval between abrasion events when a quasisteady state is reached.

The material removal rate (MRR) (which becomes constant once the quasisteady state has been reached) is given by

\[
\text{MRR} = \frac{\rho \int_{\Delta t} \text{d}M \text{d}t}{\text{pad area}}
\]  

where \( \rho \) is the total oxidation rate, including both the current density responsible for forming the first layer of Cu(I)BTA on the surface \( j_{\text{pad}} \) and the current density responsible for direct dissolution of copper ions into the solution \( j_{\text{diss}} \) (which will eventually form soluble copper complexes with glycine or the acetate buffer or as mentioned above, may reprecipitate with BTA). \( \rho \) is the atomic mass of copper, \( \text{pad area} \) is the density of copper, \( n \) is the oxidation state of the oxidized copper, and \( F \) is Faraday’s constant. However, before the integral in Eq. 3 can be evaluated using the kinetics of current decay shown in Fig. 1, it is necessary to determine where \( t_0 \) lies.

**Theoretical Analysis**

Given that the intervals between two asperity–copper contacts for typical operating parameters during CMP are around 1–10 ms, the thickness of copper that is removed between each interaction (due to both dissolution between the two interactions and removal of oxidized copper film by the interaction) is equivalent to about 0.1–1 Å. This is less than the atomic radius of copper, 1.4 Å. Because it is clearly impossible to remove a fraction of a copper atom, this low average means that the likelihood that a given surface copper species is removed in any given interaction is well below unity. The “mechanical” phenomena during copper CMP, which have hitherto been envisaged as mechanical damage to a passive film (as first proposed by Kaufman), are evidently more akin to the plucking of certain atoms or molecules from an incompletely covered surface by abrasion at any given state. This appears completely consistent with Cook’s “chemical tooth” model but suggests far less mechanical action in CMP than is considered in most models.

The small amount of material removed with each asperity–copper interaction, in conjunction with the establishment of a qua-
sisted state in the sub-monolayer regime, implies that Cu(I)BTA only covers a fraction of the copper surface betweenasperity-copper interactions and each interaction only removes a portion of this oxidized material. This situation is illustrated schematically in Fig. 4. Figure 4a shows the surface condition right before abrasion (i.e., at \( t_0 + \tau \)), and Fig. 4b shows the surface immediately after an abrasion event that removed 20% of the total adsorbed Cu(I)BTA (i.e., at \( t_0 \)). It is assumed that the Cu(I)BTA species are randomly distributed on the surface and that abrasion will remove a constant fraction of the total number of Cu(I)BTA species present on the surface. The arbitrary percentage chosen (20%) was selected for consistency with Fig. 3. The removal efficiency, \( \eta \), can be expressed as

\[
\Delta \theta = \eta \theta \quad (0 \leq \eta \leq 1)
\]

where \( \theta \) is the charge density of the oxidized copper that constitutes the Cu(I)BTA on the copper surface before abrasion.

To the best of our knowledge the kinetics for forming a monolayer of protective film in a pH 4 aqueous solution containing glycine and BTA have not been studied to date, and it would be challenging to investigate the kinetics in this regime by direct experimental measurement. The electrochemical quartz crystal microbalance (EQCM) technique has been employed to study the kinetics of forming multilayers of BTA over time scales of the order of hours. Unfortunately, the resolvable time scale of the EQCM, about 0.1 s, limits the usefulness of this technique for studying the millisecond time scale. Hence, we employed a theoretical approach using our experimental chronoamperometric data to determine the rates of dissolution of copper from bare copper sites and from the sites that are occupied by BTA and then used these data to calculate the kinetics of adsorption of BTA onto copper.

The experimentally measured current densities in Figs. 1 and 2 include current that leads to the formation of the protective film and current that leads to direct dissolution of the copper. As noted above, the total current was inversely proportional to the square root of time

\[
i_{\text{total}} = i_{\text{pass}} + i_{\text{diff}} = i_m \left( \frac{1}{t_m} \right)^{0.5} \quad \text{for} \quad t \leq t_m
\]

where \( i_m \) is the current density at \( t_m \).

The current density responsible for forming adsorbed Cu(I)BTA can be written as

\[
i_{\text{pass}}(t) = \frac{di}{dt} = \frac{c}{\theta} \frac{d\theta}{dt}
\]  

where \( \theta \) is the fractional coverage and \( c \) is a constant that relates the fractional coverage to the charge density of the oxidized copper that constitutes the Cu(I)BTA on the copper surface.

The constant \( c \) is easily evaluated. When a complete Cu(I)BTA monolayer has formed (i.e., \( \theta = 1 \)), \( q \) is equal to \( c \) (by \( q = c \theta \)). Hence \( c \) is given by

\[
c = neN
\]  

where \( n \) is unity for Cu(I), \( e \) is the elementary charge, 1.602176 \times 10^{-19} \text{C/electron}, and \( N \) is the surface density of Cu(I)BTA on the surface.

Assuming that copper dissolves directly into the solution from both bare sites and those on which BTA is adsorbed but with different potential-dependent rate constants denoted by \( a \) and \( b \), respectively, and that these rate constants are independent of the fractional coverage, \( \theta \), the current density, for the direct dissolution of copper can be written as

\[
i_{\text{diss}} = a(1 - \theta) + b \theta
\]

Combining Eqs. 5, 6, and 8 gives the following linear differential equation that governs the kinetics of BTA adsorption for \( t \leq t_m \)

\[
a(1 - \theta) + b \theta + \frac{c}{\theta} \frac{d\theta}{dt} = i_m \left( \frac{1}{t_m} \right)^{0.5} \quad \text{or}
\]

\[
\frac{d\theta}{dt} = \frac{i_m}{c} \left( \frac{1}{t_m} \right)^{0.5} + \frac{a - b}{c} \theta - \frac{a}{c}
\]

Solving the first order differential equation using the boundary condition \( \theta = 0 \) at \( t_m \) yields

\[
\theta(t) = \left[ \frac{i_m \sqrt{\pi} \sqrt{\theta}}{\sqrt{c(a - b)}} \right] \text{erf} \left( \sqrt{\frac{a - b}{c} t} \right) + \frac{a - b}{a - b} e^{-\frac{a b}{c}} - \frac{a}{a - b} e^{-\frac{a b}{c} t}
\]

From Eq. 9 and the definition of \( t_m \), it is apparent that at \( t_m \), \( \theta = 1 \) and \( d\theta/dt = 0 \), hence

\[
b = i_m
\]

This is consistent with the oxidation rate at \( t_m \) being exclusively due to the dissolution of copper from BTA adsorbed sites. The coefficient \( a \) can be determined from the oxidation rate at \( t_m \) in a solution that does not contain BTA, which is given by Fig. 2. The coefficient \( c \) can be calculated from Eq. 10 using the determined coefficients \( a \) and \( b \) and the condition at \( t_m \) (\( \theta = 1 \)). The adsorption density of BTA at monolayer coverage can then be determined from Eq. 7 and the kinetics of adsorption evaluated from Eq. 10.

For pH 4 aqueous solution containing glycine and BTA, one can use material removal rates reported in the literature to estimate the position of quasisteady state under typical conditions, assuming that the kinetics of BTA adsorption would be similar under polishing conditions to those for the microelectrode. Substituting Eqs. 5 and 11 into Eq. 3 gives

\[
MRR = \frac{M_{Cu}}{\rho n F \tau} \left[ \frac{i_{\text{pass}}}{t_m} \left( \frac{1}{t_m} \right)^{0.5} \right] dt \quad \text{or}
\]

\[
= \frac{M_{Cu} b \sqrt{\pi}}{\rho n F \tau} \left[ \frac{i_{\text{pass}}}{t_m} \right] \left( \frac{1}{t_m} \right)^{0.5} dt
\]

\[
= 2 \frac{M_{Cu} b \sqrt{\pi}}{\rho n F \tau} \left[ \left( \frac{i_{\text{pass}}}{t_m} \right)^{0.5} - \frac{a}{c} \right]
\]

Thus, knowing the parameters \( b \) and \( t_m \) for given conditions, one can determine the characteristic time \( t_c \) corresponding to the beginning of quasisteady state for a given MRR and value of \( \tau \).

Results and Discussion

The kinetics of adsorption of BTA onto a copper microelectrode at 0.6 and 0.4 V (SCE) in a pH 4 aqueous solution containing 0.01 M glycin and 0.01 M BTA (the second and third highest lines in Fig. 1) were modeled using the equations derived. The evaluated coefficients and constants are listed in Table I. Note that the ratio of coefficients \( a \) and \( b \) (\( a/b \)) and the coefficient \( c \) are similar at both
potentials, which is physically reasonable. The current density at unoccupied sites (coefficient $a$) is nearly 2 orders of magnitude higher than that at sites occupied by BTA (coefficient $b$), which demonstrates the efficacy of BTA as a corrosion inhibitor.

To further assess the validity of the derived values, the coefficient $c$ was converted into the adsorption density of BTA on copper and compared with values in the literature. An upper limit for the adsorption density of Cu(I)BTA on copper surfaces can be estimated from the surface density of the most closely packed copper surface, namely, the (111) surface, $1.77 \times 10^{15}$ atoms/cm$^2$. Xu et al. reported the surface density of a monolayer of BTA on copper surfaces from acidic aqueous solution to be $6.3 \times 10^{14}$ molecules/cm$^2$. Bastidas reported the projected area of a vertically adsorbed BTA molecule to be about 20 Å$^2$ if adsorbed with its molecular plane normal to the surface, corresponding to a saturation limit of $2.8 \times 10^{14}$ molecules/cm$^2$, and about 12 Å$^2$ if adsorbed with its molecular plane parallel to the surface, corresponding to a saturation limit of $8.4 \times 10^{14}$ molecules/cm$^2$. Xu et al. also reported the surface density of a monolayer of BTA on Cu$_2$O equilibrated with a neutral pH aqueous BTA solution to be $6.5 \times 10^{13}$ cm$^{-2}$. Bastidas reported the projected area of a vertically adsorbed BTA molecule to be about 38 Å$^2$ for the horizontal orientation of BTA, corresponding to surface densities of $5.0 \times 10^{14}$ molecules/cm$^2$ and $2.6 \times 10^{14}$ molecules/cm$^2$, respectively. Thus, the adsorption density of BTA on copper surface is between $2.6 \times 10^{14}$ and $8.4 \times 10^{14}$ molecules/cm$^2$.

The experimentally evaluated coefficient $c$ in Table I corresponds to BTA adsorption densities of $3.91 \times 10^{14}$ (at 0.6 V) and $3.89 \times 10^{14}$ molecules/cm$^2$ (at 0.4 V) on copper, intermediate between the saturation limits for BTA molecular planes parallel to the surface and normal to the surface. This implies either a range of orientations of BTA molecules in a monolayer or that each BTA molecule is adsorbed onto the surface with its molecular plane tilted with respect to the surface normal. This consistency with independently obtained data affirms the validity of the approach adopted here for determining the adsorption behavior of BTA in pH 4 aqueous solution containing BTA and glycine.

The resulting millisecond scale kinetics of adsorption of BTA onto copper surfaces from acidic aqueous solution are shown in Fig. 5, which shows rapid initial adsorption of BTA onto the copper surface. Within 30 ms (at 0.6 V), more than 90% of the copper surface is occupied by adsorbed BTA. The adsorption kinetics of BTA at 0.4 V are very similar to those at 0.6 V when plotted as a function of normalized time (i.e., $t/t_m$), despite the differences in the coefficients $a$, $b$, and $c$ (inset of Fig. 5).

Substituting the coefficients $a$, $b$, and $c$, along with the adsorption kinetics shown in Fig. 5, into Eqs. 5, 8, and 9 yields Fig. 6, which shows the current density responsible for passivation and the current density for direct dissolution of copper, plotted as a function of time during the formation of a monolayer of BTA on copper. It is evident that initially the vast majority of the current is due to the formation of the passive layer, albeit at a steadily declining magnitude. (It should also be recognized that this portion of Fig. 6 is extrapolated, since capacitive charging dominated the current observed in the experimental potential-step chronocoulometry experiments.) At around 0.1 ms the current due to direct dissolution of copper becomes comparable to that due to the formation of the passive layer, and by 1 ms the majority of the current is due to direct dissolution of copper.

Equation 14 was solved numerically for the different parameters of $b$ and $t_m$ corresponding to potentials of 0.6 and 0.4 V, using the atomic weight of copper (63.54 g/mole) and density (8.96 g/cm$^3$). The value of $n$ was taken as 2 because although copper is in the +1 oxidation state in adsorbed Cu-BTA complexes, it enters solution in the +2 oxidation state. Two extreme values of material removal rates taken from the literature were considered, namely, 130 and 600 nm/min. Two extreme values of $\tau$ were also considered, namely, 1 and 10 ms, values representative of typical pads and rotational velocities. The resulting values of $t_m$ are reported in Table II, along with the values of $\theta$ corresponding to these times, and the...
values of $\theta$ at $t_n + \tau$. There was no physically realistic solution to Eq. 14 for the higher value of $\tau$ in conjunction with the higher material removal rate. Physically it is reasonable that high material removal rates would not be seen with slow rotational speeds in CMP. It is seen that for the lowest material removal rates typically encountered in copper CMP, the surface is almost completely covered by BTA throughout the polishing process. The fractional coverage is about 93% at 0.6 V (SCE) and 88% at 0.4 V (SCE), and only a miniscule amount of BTA is removed with each asperity–copper interaction. Under such conditions, essentially all material is removed by direct electrochemical dissolution of copper. Conversely, at the highest material removal rates typically encountered in copper CMP, the copper surface undergoing active polishing is only partially covered by BTA. (Of course recessed areas on the copper surface that do not interact with the pad would be fully protected by thick BTA layers.) Immediately after an asperity–copper interaction, about 64 and 49% of the sites on copper would be occupied by BTA at 0.6 and 0.4 V, respectively. These occupancy values would have increased to 71 and 61% after just 1 ms. These conditions correspond to values of $t_n$ of around 1 ms, which from Fig. 6 is the time at which material removal involves both direct dissolution and formation of passive layers. Regardless of the precise material removal rate, it is clear that dissolution is an important material removal mechanism.

Conclusions

The millisecond scale adsorption kinetics of BTA onto copper surfaces in pH 4 aqueous solution containing 0.01 M glycine and 0.01 M BTA have been determined from analysis of potential-step chronoamperometry data. These kinetics show that BTA rapidly adsorbs onto copper surfaces, forming a monolayer of Cu(I)BTA within a second or so. Building on this analysis, we have shown that under typical CMP conditions, with typical material removal rates, copper surfaces undergoing active polishing in acidic slurries containing BTA have less than a monolayer of BTA on the surface. Further, only a small proportion of the adsorbed BTA is removed with any given asperity–copper interaction; most material removal is due to direct dissolution of Cu$^{2+}$ ions (which may subsequently form complexes with other slurry components) into the slurry. This mechanistic picture of copper CMP differs from the commonly accepted model first depicted schematically by Kaufmann et al.\textsuperscript{3} for polishing tungsten, involving thick passive layers that are completely removed with each interaction. We have also confirmed that as proposed earlier,\textsuperscript{9} CMP in acidic conditions in the presence of BTA is a wear-induced corrosion process rather than a corrosion-enhanced wear process.

Acknowledgments

This work was supported in part by the UC Discovery Grant ele07-10283 under the IMPACT program and AMD, Applied Materials, ASML, Cadence, Canon, Ebara, Hitachi, IBM, Intel, KLA-Tencor, Magma, Marvell, Mentor Graphics, Novellus, Panoramic, SanDisk, Spanson, Synopsys, Tokyo Electron Limited, and Xilinx, with donations from Photronics and Toppan.

The University of California, Berkeley assisted in meeting the publication costs of this article.

References