An easy way to prepare layered nanoplatelets: Fragment of nanostructured multilayers

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An easy way to prepare layered nanoplatelets: Fragment of nanostructured multilayers

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In this study, we present an easy way to create layered-nanoplatelets with well-defined geometry by controlling the cracking process of nanostructured multilayers. The geometrical dimension of layered-nanoplatelets is determined by the multilayer intrinsic size, the total strain, and the elastic mismatch between the substrate and multilayers, which was analyzed by statistical approach. Fracture behaviors characterized by critical strain to nucleate microcrack, fracture toughness, and evolution of fragment width were also studied for nanostructured Cu/Cr multilayers with modulation period (λ) spanning from 5 to 250 nm and were quantified based on linear elastic theory and shear-lag theory. An optimal modulation period seems to be likely favorable for maximizing the ductility, strength, and fracture toughness of the nanolayered materials. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4728178]

I. INTRODUCTION

The mechanical integrity and the stability of thin films/multilayers are key issues to the reliability of flexible microelectronics (e.g., paper-like displays) and the nanotechnological application (e.g., production of thin nanoplatelets), which have been studied extensively involving experimental observations and theoretical analysis. Recently, the “electric resistance change” method (ERCM) was used to in situ identify the microcracks nucleation and related failure mechanisms in polymer-supported Cu-based multilayers. However, the subsequent fragment of multilayers is quite critical to produce defined thin nanoplatelets, which has not been well studied yet. In the present work, we study the fracture behavior of polymer-supported Cu/Cr multilayers by uniaxial tensile test. The fragment processes are quantitatively characterized by statistical method, and the fracture toughness was respectively estimated by the linear elastic theory and the shear-lag theory. The understanding of the principles of the cracking process allows us to present guidelines for the controlled fabrication of nanoplatelets.

II. EXPERIMENTAL METHODS

500 nm-thick Cu/Cr multilayers with modulation period (λ = 2h, h is individual layer thickness) spanning from 5 to 250 nm were synthesized by means of direct current (DC) magnetron sputtering at room temperature on 125 μm-thick polycrystalline foils (Kapton 500HN by DuPont, Circleville, OH) with measured elastic modulus ~3.9 GPa. In film deposition, the first layer on the polymer substrate was Cr and the last layer was Cu. High-resolution transmission electron microscopy (HRTEM) observation was performed using a JEOL-2100F TEM with 200 kV, accelerating voltages to observe the modulation structure and the interface structure. More details about the microstructure of Cu/Cr multilayers can be found in Ref. 5. The residual tensile stresses of as-deposited Cu/Cr multilayers measured by using “sin^2 ψ method” were ~200 ± 100 MPa and insensitive to λ, which is far lower than their yield strength. In this method, the strain ε = σ is defined as the difference in the interplanar spacing d for stress free and stressed lattice, as given in Eq. (1). This strain was measured along laboratory coordinate axes, perpendicular to a particular (h k l) plane used in the coordinate axes and expressed in terms of stress after assuming that the film is isotropic and the stress state is biaxial and inserting Hook’s law. The resultant equation takes a simple form of Eq. (1) and residual stress in the film is calculated using

\[ \varepsilon = \frac{d_{\phi \psi} - d_0}{d_0} = \frac{1 + \nu}{E} \sin^2 \psi - \frac{\nu}{E} (\sigma_{11} + \sigma_{22}), \]

where d_{\phi \psi} is the lattice spacing of (h k l) planes tilted by and rotated by ψ within the plane of the film with respect to axes σ_{11}, and d_0 is the strain free lattice spacing. The terms E, ν, and σ_{11} are the elastic constant, Poisson ratio, and normal stress in the direction ψ, respectively. From the plot of d_{\phi \psi} vs. sin^2 ψ, the residual stress in the Cu layer (σ_{Cu}) and Cr layer (σ_{Cr}) can be, respectively, calculated from the slope of the line. Data was taken at ten different tilts for getting accurate d spacing shift. The total residual stress of the multilayers, \( \sigma_m \), is finally determined by simply averaging on the two constituent layers as

\[ \sigma_m = \frac{h_{Cu} \sigma_{Cu} + h_{Cr} \sigma_{Cr}}{h_{Cu} + h_{Cr}}, \]

where \( h_{Cu} \) and \( h_{Cr} \) are the thickness of the Cu layer and Cr layer, respectively.

The dog-bone shaped samples with a gauge section of 30 mm in length and 4 mm in width were uniaxially stretched to strain \( \varepsilon = 30\% \) at a constant strain rate of 1 × 10^{-4} s^{-1}. 

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using a Micro-Force Test System (MTS® Tyron 250) at room temperature. The simultaneous measurement of electrical resistance change of metallic multilayers was useful to exactly identify the critical crack nucleation strain $e_C$ of multilayers (called in situ-ERCM hereafter), for which the experimental details can be referred to Refs. 3, and 5–7. For these conductive films, an important advantage is that the electrical resistance is very sensitive to the presence of the smallest cracks, which may well be undetectable under the microscope. After the Cu/Cr NMMs stretched to a given strain, the sample was unloaded from the tensile stage and then the typical cracking morphologies of the sample were ex situ observed to statistic the microcrack density (MCD, total length of the perpendicular microcracks per unit area, denoted as $S$). Extrapolation treatment was subsequently employed to determine the critical strain to nucleate microcrack $e_C^M$ at $S = 0$ (called ex situ-MCDM hereafter).

III. RESULTS AND DISCUSSION

The typical cracking morphologies of Cu/Cr multilayers tested at different strains were shown in Fig. 1. When the applied strain ($\varepsilon$) reaches a critical value ($e_C$), the cracking of the multilayers perpendicular to the loading direction will begin [as shown in Fig. 1(a)]. With increasing applied strain, the number of the cracks increases and the roughly uniform spacing can be observed [see Fig. 1(b)]. At very large strain ($\varepsilon > \sim 20\%$), the tensile test leads to the buckling, while the microcrack density $S$ saturates [see Figs. 1(c) and 1(d)]. When $S$ is saturated, further increase in applied strain only results that $S$ drops and crack opening distance $\delta$ increases.

With increasing $\varepsilon$, three stages of fragment, i.e., random cracking [Fig. 1(a)], to midpoint cracking [Fig. 1(b)] and delamination and buckling [Figs. 1(c) and 1(d)] can be observed, as is consistent with the $S$-$\varepsilon$ curve shown in Fig. 2(a). On straining up to $5\%$–$7.5\%$, $S$ increases rapidly with increasing $\varepsilon$. After a steep ascent, the slop of the $S$-$\varepsilon$ curves changes gradually. At very large strain, $S$ reaches a saturation value $S_S$, see Fig. 2(a). One can also clearly see that the critical strain $e_C^M$ is very close to $e_C$ and strongly depends on $\lambda$, as shown in Fig. 2(b). Interestingly, over this $\lambda$ range the $e_C$ of the multilayers increases first, followed by a peak at a critical $\lambda^* \approx 50$ nm. Below $\lambda^*$, $e_C$ decreases with reducing $\lambda$, similar to the behavior of single-layer films, while above $\lambda^*$, a smaller $\lambda$ leads to higher $e_C$. The underlying reasons for the nonmonotonically varies of $e_C$ can be attributed to the suppression effect of the ductile Cu layer on propagation of microcracks initiated in the brittle Cr layer.

Corresponding to the MCD $S$, the fragment kinetics, i.e., evolution of mean crack distance (or mean fragment width (MFW)) $L$ ($L \approx 1/S$) also displays three characteristic regimes when plotted in double logarithmic scales shown in Fig. 3(a). In all of regimes, before and after the change in slope, the power-law functions in the form of $L = c\varepsilon^{-k}$ can be used to fit the experimental data, where $c$ is a constant value and $k$ is the exponents obtained by least-squares fit procedure, which indicates the fragmentation rate, i.e., the rate of crack generation. In the first two regimes, $k \neq 0$ whereas in the third regime, $k = 0$.

In the first random cracking regime, one can see that uniaxial tensile load leads to a rapid decrease in MFW. Owing to the interaction between cracks is negligible, the

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**FIG. 1.** Optical micrographs showing the microcracks evolution processes for Cu/Cr multilayers with modulation period $\lambda = 10$ nm with different strains (a) 5%, (b) 10%, (c) 20%, and (d) 30%. The loading axis is the horizontal direction in the images.

**FIG. 2.** (a) The mean perpendicular microcracks density $S$ of Cu/Cr multilayers with $\lambda = 10$ nm as a function of the strain $\varepsilon$, inset shows the dependence of electrical distance change $\Delta R/\Delta R_0 = (R - R_0)/R_0$ on strain $\varepsilon$ for $\lambda = 10$ nm Cu/Cr multilayers, illustrating for determining the critical strain by using both statistical microcrack density changes and electrical resistance change method. (b) Dependence of $e_C$ determined by statistical microcrack density changes (half circles) and electrical resistance change (half square dots) method on $\lambda$ for Cu/Cr multilayers.
rate of crack generation is governed solely by the multilayer strength distribution and the crack location is determined by the defect distribution in the multilayer. After that, the fragmentation rate decreases significantly in the second midpoint cracking stage and concomitant slow decrease in MFW. It can be ascribed that fragment width (FW) become small compared with twice of the critical length leading to the maximum stress in a fragment cannot reach the unperturbed far-field level.9 At macroscopic strain $\varepsilon \geq 15\%–20\%$ (in third adhesive failure regime), the MFW remains approximately constant at a saturated MFW and the fragmentation rate virtually stops. The intersection of the two power-law functions was used to define the critical strain $\varepsilon_T$ as the transition strain for fragmentation rate transformation and optimum MFW $L_T$ for perpendicular microcrack, respectively. In the same way, the saturation strain for perpendicular microcracks $\varepsilon_S$ and final MFW $L_S (L_S \approx 1/S_S)$ can also be respectively defined, as shown in Fig. 3(a).

Handge and coworkers12,13 have pointed out that for thin brittle films on compliant substrates $k_1$ and $k_2$ are related to the strength distribution in the film and that $k_1$ is equal to the Weibull exponent $\alpha$ for the strength distribution of the brittle film and $k_2$ depends on both $\alpha$ and $\beta$, where $\beta$ is the nonlinearity parameter of the strain transfer between film and substrate, according to

$$k_2 = \frac{\beta \alpha}{(\beta + 1)\alpha + 1} = \frac{\beta k_1}{(\beta + 1)k_1 + 1}.$$  \hspace{1cm} (3)

For $\beta = 0$ the interfacial stress is constant. The case $\beta = 1$ for a linear elastic stress/strain transfer (corresponds to Hook’s law). For $\beta > 1$ the stress–strain relation has an increasing secant modulus, whereas $0 < \beta < 1$ suggests the elastic part of stress-strain curve for materials which have a yield point. Using the experimental values for $k_1$ and $k_2$, we can experimentally determine the parameters for Weibull distribution of defects and the nonlinearity parameter $\beta$ standing for the nature of strain/stress transfer between multilayer and substrate. Based on the Eq. (3) and using the experimental values of $k_1$ and $k_2$ (as listed in Table I), $\beta$ is found to be between 0.7 and 1 for Cu/Cr multilayers. It indicates that the stress/strain transfer between the multilayer and polyimide substrate is not purely but mainly linear elastic in cracking process, additional stress relaxation mechanisms, such as substrate deformation and dislocation plasticity of multilayer, probably take place.19,20

Begley et al.17,18 have developed a quasi-analytical cracking model, describing the relationship between the average macroscopic stress ($\sigma$) and macroscopic strain ($\varepsilon$) of the multilayer, the mean fragment width ($L$), crack opening displacement ($\delta$), and the steady-state energy release rate.
(G_{SS}) for channeling crack formation, for the multilayers comprised of ultra-thin stiff films on highly compliant substrates. According to this model the effective modulus $E$ of the cracked film/substrate composite is lower than that of the intact sample $E_0$ and reduces with increasing crack density (or decreasing crack distance)\(^{(7, 14)}\):

$$E = E_0 \left[ 1 + 0.22 \left( \frac{h_m E_m}{L \varepsilon_s} \right) \left( \frac{h_m E_m}{h_s E_0} \right)^{-1} \right], \quad (4)$$

where $E$ is the Young’s modulus of the multilayers, whose value can be determined from the stress-strain curves of the multilayer, $h$ is the thickness, $h_m = h_m/(h_m + h_s)$, $h_s = h_s/(h_m + h_s)$, $E_m = E_m/(1 - \nu_m^2)$, $E_s = E_s/(1 - \nu_s^2)$, and $E_0 = h_m E_m + h_s E_s$. The subscripts $s$ and $m$ stand for substrate and multilayers, respectively. The pre-factor 0.22 has been determined from finite element models. Based on these studies,\(^{(17, 18)}\) the crack opening displacement $\delta$ can be given as

$$\delta = 0.22 h_m \left( \frac{E_m}{E_s} \right) \left( \frac{E(L_x)}{E_0} \right) \varepsilon, \quad (5)$$

where $\varepsilon$ is the total strain imposed on the multilayer.\(^{(17)}\) The stress in the intact multilayer (prior to cracking) is approximated as $\sigma_m(L_0) = E_m \varepsilon$. If one assumes a uniform crack opening displacement throughout the thickness of the film, the energy release rate $G_{SS}$ is given by\(^{(18)}\):

$$G_{SS} = \sigma_m(L_0) \delta(L_x) = 0.22 \left( \frac{E_m}{E_s} \right) \left( \frac{E(L_x)}{E_0} \right) \varepsilon(L_x) h_m \sigma_m(L_0), \quad (6)$$

where $\sigma_m(L_0)$ is the stress in the intact portion of the multilayer, $E(L_x)$ is effective modulus of the cracked multilayer at MFW with $L_x$, and $\delta(L_x)$ and $\varepsilon(L_x)$ are the crack opening and total strain after the formation of the final set of cracks. In order to apply these equations to our experimental data we use the crossover values $L_T$ and $\sigma_T$ for $L_t$ and $\varepsilon(L_t)$ as well as $\sigma_m(L_0) = E_m \varepsilon c$ for $\sigma_m(L_0)$ to obtain $G_{SS}^C$. If at the onset of cracking, i.e., $\varepsilon = \varepsilon c$, $G_{SS}$ can be approximated as

$$G_{SS} = G_{SS}^C \approx 0.22 \left( \frac{E_m \varepsilon c}{E_s} \right) h_m, \quad (7)$$

where the symbols have the same meaning as before. The fracture toughness, hence, can be obtained by\(^{7}\):

$$K_{IC} = \sqrt{\frac{E_m G_{SS}^C}{1 - \nu_m^2}}, \quad (8)$$

Base on our experimental results, $K_{IC-Blethy}$ and $K_{IC-Blethy}$, respectively, varies in 5–12 MPa.m\(^{1/2}\) and 2–9 MPa.m\(^{1/2}\), as shown in Fig. 3(b). For comparative reasons, we calculated $K_{IC-Blethy}$ based on linear elastic fracture mechanics developed by Beuth,\(^{8}\) in which the energy release rate $G_{SS}$ can be expressed as

$$G_{SS}^C = \frac{\pi \sigma^2 h_m}{2E_m} (1 - \nu_m^2) g(\xi, \zeta), \quad (9)$$

where $\sigma$ is the tensile stress of the films at the critical point of $\varepsilon_c (\varepsilon = E_m \varepsilon c)$, $g(\xi, \zeta)$ is a dimensionless quantity that can be calculated from the elastic mismatch between the film and substrate, with $\xi$ and $\zeta$ being the two Dundurs’ parameters,\(^{8}\) and other symbols have the same meaning as before. For our case, $g(\xi, \zeta)$ is estimated (through interpolation method) according to Ref. 8. Using experimental data together with Eqs. (8) and (9), the calculated $K_{IC-Blethy}$ as a function of $\lambda$ is also plotted in Fig. 3(b). It is found that the maximum fracture toughness reached at $L_c \approx 50\text{nm}$ and that the $K_{IC-Blethy}$ somewhat higher than that of $K_{IC-Blethy}$, indicating the substrate does play some role in the fracture process of multilayers.

The size distribution of the final platelets is highly relevant for technological applications. Due to randomly distributed defects, FWs are statistically distributed as well. In Fig. 3(c), we plot the distribution of the FWs $L$ for multilayers with $\lambda = 10\text{nm}$ at different applied strains. To compare the distribution for different applied strains, we rescaled the distribution with respect to its experimental value $L_T$ and plot it as a function of $(L/L_T)$, $g(L)$ is a probability distribution function of the FWs $L$ that can be approximated by a two-parameter Weibull distribution with the cumulative form\(^{11}\):

$$P(L) = 1 - \exp[-(aL)^b], \quad (10)$$

and the fit parameters $a > 0$ and $b > 0$, where $a$ is the scale parameter for fragment width and $b$ is the shape parameter of the distribution. Note that a large value of Weibull exponent $b$ corresponds to a narrow distribution. Fig. 3(c) reveals that the relative width of the distribution varies monotonically with the applied strain, i.e., the narrowest distributions can

<table>
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<th>$i$ (nm)</th>
<th>250</th>
<th>125</th>
<th>100</th>
<th>62.5</th>
<th>50</th>
<th>25</th>
<th>10</th>
<th>5</th>
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<tbody>
<tr>
<td>$\sigma_T$ (%)</td>
<td>3.53</td>
<td>3.74</td>
<td>3.83</td>
<td>3.93</td>
<td>4.25</td>
<td>4.73</td>
<td>3.85</td>
<td>3.94</td>
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<tr>
<td>$L_T$ (nm)</td>
<td>24.8</td>
<td>29.4</td>
<td>32.9</td>
<td>33.1</td>
<td>33.7</td>
<td>30.8</td>
<td>26.1</td>
<td>22.3</td>
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<tr>
<td>$h$</td>
<td>2.16 ± 0.35</td>
<td>2.38 ± 0.45</td>
<td>2.27 ± 0.35</td>
<td>2.43 ± 0.4</td>
<td>2.55 ± 0.25</td>
<td>2.75 ± 0.3</td>
<td>2.98 ± 0.35</td>
<td>3.24 ± 0.4</td>
</tr>
<tr>
<td>$k_1$</td>
<td>2.99 ± 0.37</td>
<td>3.42 ± 0.38</td>
<td>3.53 ± 0.44</td>
<td>3.78 ± 0.43</td>
<td>4.27 ± 0.47</td>
<td>3.92 ± 0.52</td>
<td>3.38 ± 0.3</td>
<td>3.75 ± 0.37</td>
</tr>
<tr>
<td>$k_2$</td>
<td>0.37 ± 0.04</td>
<td>0.38 ± 0.06</td>
<td>0.42 ± 0.03</td>
<td>0.39 ± 0.05</td>
<td>0.44 ± 0.07</td>
<td>0.41 ± 0.05</td>
<td>0.35 ± 0.02</td>
<td>0.37 ± 0.05</td>
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<tr>
<td>$\Gamma$</td>
<td>0.942</td>
<td>0.948</td>
<td>0.951</td>
<td>0.959</td>
<td>0.965</td>
<td>0.958</td>
<td>0.931</td>
<td>0.926</td>
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<td>$\sigma_m$ (MPa)</td>
<td>580</td>
<td>775</td>
<td>863</td>
<td>1013</td>
<td>1347</td>
<td>833</td>
<td>420</td>
<td>310</td>
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<tr>
<td>$\tau$ (MPa)</td>
<td>26.77</td>
<td>30.15</td>
<td>32.00</td>
<td>31.48</td>
<td>39.47</td>
<td>29.82</td>
<td>18.86</td>
<td>19.94</td>
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**TABLE I.** Summary of results for crossover values for the transition strain $\sigma_T$ and optimum mean fragment width $L_T$, Weibull exponent for fragment width $b$, two scaling exponent $k_1$ and $k_2$, values of $\Gamma$ and tensile strength $\sigma_m$, interfacial shear strength $\tau$.
be found in the largest strained multilayers. In other words, with increasing strain, the larger fragments break leading to narrowing the FW, and a minimum shift of the smaller FW. Subsequently, a regular shifting of the distribution curve toward smaller FW is observed. In terms of FW as a function of strain, this corresponds to the crossover between the first and second power law. The decrease of FW with strain allows for the proper selection of a desired FW within a range spanning half an order of magnitude.

At very high strains, an additional cracking mode is observed, namely, cracking parallel to the loading direction caused by delamination and buckling. This mode is considered to be a secondary effect: by cracking, the film is unloaded substantially, and thus, unlike the substrate, shows no transverse contraction parallel to the primary cracks. As the substrate does contract, it induces a compressive stress in the multilayers, due to mismatch in Poisson’s ratios between film and substrate. It is revealed in Fig. 3(d) that the final fragment length, $L_f$, is the minimum FW at saturation, and other symbols have the same meaning as above. The $L_f$ is not a measurable quantity and was related using a stochastic failure approach to $L_S$: $L_f = 1.5 L_S$. The $L_S$, thus, is directly proportional to $\sigma_m$, i.e., $L_S = \frac{4h_m \sigma_m}{\tau}$.

The tensile strength $\sigma_m$ of brittle materials showing Weibull-type failure mechanism is defect controlled and exhibits size-dependent effects, which can be written as a two-parameter equation:

$$\sigma_m = \frac{1}{c} \left( \frac{L_S}{L_0} \right)^{-\frac{1}{\gamma}} \Gamma(1 + 1/z),$$  \hspace{1cm} (12)$$

where $z$ is again the Weibull exponent, $\Gamma$ is the gamma function. For Cu/Cr multilayers, $z$ and $\gamma$ are derived from a linear approximation of the initial part of the fragmentation diagram, where $\tilde{L}$ as a function of $\varepsilon$, in logarithmic coordinates [see Fig. 3(a)], and the scale parameter for strength was obtained by multiplying that for strain $\varepsilon_C$ by the Young’s modulus of multilayers. The interfacial shear strength, thus, obtained by combining Eqs. (11) and (12) is almost a constant about $30 \pm 10$ MPa within the scatter. The maximum $\sigma_m \sim 1347$ MPa also appeared at $\lambda_C \approx 50$ nm. Furthermore, from Fig. 3(f) one can find that the distribution of the fragment length $l$ of the platelets also follows the two peaks distribution (got from the Gaussian peak-fitting results). A detailed investigation of the delamination and buckling of the multilayers is worthy of a focused separate study and is outside the scope of this work.

IV. SUMMARY

In the present work, we investigate sequential cracking in Cu/Cr multilayers on polymer substrates to show how multiple cracks evolve in a brittle metallic multilayers as a function of layer thickness and total strain. The combination of these findings leads to a process that can be used to fabricate nanoplatelets in a controlled manner. An optimum size distribution is found at the crossover particle size $L_T$. Peak values are observed for the ductility, tensile strength, and fracture toughness at $\lambda$ of 50 nm. The optimum mechanical properties can be achieved in nanolayered materials.

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