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Mechanical response of ALD alumina coatings on stiff and compliant substrates

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In this study the mechanical properties of ALD alumina coatings deposited at a range of temperatures from 80°C onto substrates with differing stiffness including hard, stiff materials (silicon and glass) and soft, compliant materials (PET) have been investigated by nanoindentation. Approaches necessary to extract coating properties from the coating/substrate composite data have been developed in order to obtain reliable data from 150nm thick coatings on hard, stiff substrates. This has shown that the elastic modulus of ALD alumina increases with deposition temperature as might be expected from the variation in density. Measurements for the ALD alumina coatings on PET using the same analysis method give lower elastic Modulus and hardness values; this is not due to an intrinsic difference in coating properties but is a consequence of the effect of modulus mismatch between coating and substrate on the measurement method. Reliable data for the coatings on PET are therefore more difficult to obtain but can be determined if a suitable modelling approach is adopted.

I. INTRODUCTION

Atomic layer deposition (ALD) is a thin film growth technique which is based in a sequence of self-limiting surface reactions which build up a coating in a layer by layer manner. In a typical process for a simple AB compound two gas phase molecules are exposed to the substrate surface in an alternating fashion such that the A gas reacts with surface species and adds the first desired element and subsequently the B gas reacts with the new surface species created to add the second desired element. The second reaction also recreates the initial surface species so that the A gas reaction may start again. ALD alumina using $\text{Al}(\text{CH}_3)_3$ and water is one of the most commonly studied ALD systems. The mechanical response of reasonably thick ($>200\text{nm}$) ALD alumina deposited at temperatures above 100°C on hard, stiff substrates has been investigated by several workers using a range of techniques including cantilever bending and nanoindentation¹⁻⁴. However, many applications of ALD coatings (e.g. OLEDs) require the coating of flexible, compliant substrates at lower deposition temperatures to lower thickness and there is a need to measure reliable mechanical property data for use in design and for quality assurance purposes.

Nanoindentation is a versatile technique for assessing the mechanical response of very thin coatings⁵. In this test an indenter with known geometry is loaded against the test sample and a continuous record of load and indenter displacement is recorded; from this load displacement curve mechanical properties of the sample such as hardness and Young's modulus can be determined based on the accepted approach of Oliver and Pharr⁶ which is the basis of an international standard (ISO14577). Although this method is good there are a number of circumstances which lead to inaccuracy in the data, particularly for

coated systems. With the best commercially available indenters it is possible to get very reliable data for coatings as thin as 100nm when they are deposited on a hard, stiff substrate such as sapphire or glass. However, to measure the properties of a coating independent of the substrate is a challenge if coatings get thinner or the substrate stiffness is reduced⁷. This is because it is necessary to ensure that plastic deformation occurs in the coating before it occurs in the substrate if the standard analysis methods are to be used. It is usually assumed that the indenter penetration must be less than 10% of the coating thickness to measure the hardness of the coating alone and for very thin coatings and blunt tips no plastic deformation may be observed until much higher penetrations are achieved and thus plastic deformation is largely in the substrate. In such cases a modelling approach is necessary to extract coating hardness. For elastic properties the effect is even more extreme – the coating and substrate behave as springs in series and there is a substrate contribution to the measured contact modulus at all contact scales since elasticity is a long range property compared to plasticity. In fact ISO14577 recommends that to assess the coating properties nanoindentation data be determined at a range of contact scales and the results extrapolated to zero contact depth to assess coating properties. For assessing soft coatings it recommends that data where a/t is less than 1.5 be used where a is the contact radius and t is the coating thickness. For assessing hard coatings the criterion is that data in the range $a/t < 1.5$ should be used. For an ideally sharp Berkovich indenter $a = 2.79h_c$ where h_c is the contact depth of the impression and these criteria can be rewritten as $h_c/t < 0.7$ for soft and 0.5 for hard coating extrapolation. The reliability of this approach for thin ($t \sim 150\text{nm}$) ALD alumina coatings has been assessed in this study.

When coatings are deposited on very compliant substrates like polymers the elastic deformation of the substrate can be considerable and it usually dominates the indentation measurement. Whereas some useful data can be obtained at low loads where coatings have not cracked the elastic mismatch between coating and substrate often leads to through-thickness fracture and a rapid reduction in the hardness and stiffness of the coated system. This leads to apparently low values of hardness and Young's modulus when the extrapolation method is applied, particularly if data is not obtained at sufficiently low loads and indenter penetrations. In this study we have explored the validity of nanoindentation data determined from ALD alumina coatings deposited on compliant polyethylene terephthalate (PET) substrates in the same deposition run as coatings deposited on the harder stiffer substrates mentioned above.

II. EXPERIMENTAL

A. Samples tested

ALD alumina coatings were deposited onto soda-lime glass, silicon and PET substrates using the trimethyl aluminium/water vapour approach⁸ in the same run. Films were grown in a Cambridge Nanotech Savannah 100 operated in a simple vapour-draw mode. The reactor consists of a dual heater zone platen capable of accommodating samples up to 100mm in diameter. The system is pumped with a rotary vane pump, using mineral oil (rather the Fomblin) to avoid reaction with the methyl-ligand byproduct and back streaming of carbon contamination. The semiconductor grade trimethyl aluminium (TMA, SAFC Hitech) was held at 25°C throughout. The DI water source was degassed and held at ambient. Dry high purity argon was employed as the purge gas throughout.

Depositions runs on polymer and glass substrates were performed without pre-treatment. The ALD cycle comprised of: [TMA / purge / H₂O / purge] cycles of doses [0.02s / 2s / 0.01s / 2s]. 2000 cycles were run for samples at both temperatures. Deposition runs were carried out at 80°C and 150°C; both temperatures were low enough to ensure that there was no degradation of the PET substrate. The silicon samples were included so that spectroscopic ellipsometry measurements of thickness could be made – by this approach the coating thickness on silicon was 150nm at 80°C and 160nm at 150°C. The growth rate was 0.15nm/cycle at 150°C but increased to 0.5nm/cycle at 80°C implying that conditions of single layer by layer growth were not maintained at the lower temperature. It is expected that water was condensed on the substrate at 80°C, and later TMA dosing reacts with water which was not bonded to the substrate creating a CVD reaction. To avoid this CVD reaction, a longer purging time for both of the precursors would have been necessary but this does not completely remove the condensed water at practical cycle times so it was not used in this study.

The PET sample has a glass transition temperature around 70°C and therefore its structure and properties may have changed during the ALD coating cycle. For this reason uncoated PET films were subjected to the same thermal cycle in a vacuum furnace for the two deposition temperatures and these were then used to determine the substrate data presented in this paper.

B. Coating characterisation

The composition of the coatings on glass and PET was measured by Rutherford Backscattering. Spectra were obtained at normal ion beam incidence and an incidence angle of ~70° to facilitate data fitting using the IBA Datafurnace software⁹. For the coatings deposited at 150°C stoichiometric alumina coatings were produced but the lower temperature deposition resulted in a more contaminated film containing a significant amount of carbon and hydrogen. Phase analysis was attempted using x-ray diffraction but

the coatings deposited on all samples were amorphous. Surface roughness of the samples before and after coating was determined by atomic force microscopy in a 10x10µm area.

C. Nanoindentation testing

All samples were attached to a steel block using a cyanoacrylate adhesive prior to nanoindentation testing to ensure that the compliance of the support did not contribute to the measured data. The steel block was mounted on the magnetic sample stage of a Hysitron Triboindenter fitted with a general purpose Berkovich indenter for nanoindentation testing. The Berkovich tip had a stabilised end-shape with an average radius of about 150nm determined during tip end-shape calibration using a fused silica sample according to the method of Oliver and Pharr⁶. The indenter tip was carefully calibrated before testing the ALD coated samples and then recalibrated immediately afterwards to see if any changes had taken place; none were observed. According to the Oliver and Pharr method the contact area for a given contact depth, $A(h_c)$, can be described by a function of the form

$$A(h_c) = C_0 h_c^2 + C_1 h_c + C_2 h_c^{1/2} + C_3 h_c^{1/4} + C_4 h_c^{1/8} + \text{higher terms} \quad (1)$$

Where the C_n are constants – a five term fit was used here. The contact depth, h_c , i.e. the depth at which the indenter is in contact with the material when corrected for elastic deformation of the sample is given by

$$h_c = h_{\max} - \varepsilon \frac{P_{\max}}{S} \quad (2)$$

Where $h_{\max}$ is the maximum indenter displacement, $P_{\max}$ the peak load, S the unloading stiffness (i.e. the slope of the unloading curve at the start of unloading) and ε is a constant taken to be 0.75 in this study.

If it is assumed that the tip consists of a pyramidal indenter with a spherical cap at the tip then when the contact depth is less than 9nm the indentation is only being made with the spherical cap which typically occurs when the peak load is of the order of 100 μ N on the stiff substrates. In such cases simple Hertzian contact mechanics can be used to assess the location where plastic deformation is likely to start; using the elastic properties of the glass substrate the depth of the maximum shear stress is ~20nm below the surface which is well within the coating thickness and that plastic deformation will start in the coating.

The samples were left in the Triboindenter cabinet for 24 hours prior to nanoindentation testing to allow their temperature to stabilise and equilibrate with the surroundings. Indentations were performed under displacement control with loading and unloading displacement rates of 100nm/s and a 4s hold at peak load. These test conditions reduced the effect of time-dependent deformation on the results. A 1.9 μ N contact load set point was used to identify engagement with the substrate. A 40s hold at this load prior to each indentation was used to allow stabilisation of the system; the displacement in the last 20s of this hold was used to determine the thermal drift rate; all load displacement curves were corrected for thermal drift prior to calculation of hardness and contact modulus by the method of Oliver and Pharr⁶. The tip was then removed to a height of 10nm above the surface before the indentation cycle was started. A minimum of 50 indentations were made on each sample at peak displacements from 5 to 500nm – indents were spaced at 10 micron intervals to ensure that no overlap between their deformation fields was produced. For comparison with data from other measurement techniques the Young's Modulus can be determined from the contact modulus, E_c , if the Poisson's ratio of the coating is known using

$$\frac{1}{E_r} = \frac{1-\nu_i^2}{E_i} + \frac{1-\nu_s^2}{E_s} \quad (3)$$

where E_i and ν_i are the Young's Modulus and Poisson's ratio of the indenter and E_s and ν_s are the same properties of the specimen. Usually $E_i=1141\text{GPa}$ and $\nu_i=0.07$. The value of ν_s must be measured independently if the Young's Modulus is to be calculated. An estimate of $\nu_s=0.24$ may be made for an amorphous alumina coating¹⁰ but, in the absence of measured values for the coatings tested here, results will be discussed only in terms of the contact modulus, E_r .

Hardness and contact modulus data were plotted as a function of contact depth and extrapolated to zero depth to determine the coating properties following the ISO standard approach¹¹. One key choice is the amount of data to be included in the extrapolation – since the ISO standard recommends a linear extrapolation it is necessary to select data where there is no rapid, non-linear change in the measured results. In general this involves limiting the extrapolation to low penetration data dominated by the coating. In this study limits were used to define the extrapolate range to where the contact depth is less than 20% of the coating thickness for hardness and 10% for contact modulus which is somewhat lower than recommended in the standard. The reason for this deviation is that through-thickness fracture in the coating can lead to a change in slope of the hardness or modulus versus contact depth plots with values rapidly approaching that of the substrate. In such cases it is possible to use two extrapolation lines to extract both coating and substrate properties (Figure 1). This fracture behavior usually occurs after the penetrations where the spherical cap of the indenter dominates behavior but when the indenter edges have contacted the film. It is also necessary to remove the data points at

the lowest penetrations where full elastic-plastic indentation behaviour had not been established when assessing coating hardness.

The Hysitron Triboindenter allows AFM imaging of the indented surface using the tip that made the indent. This imaging was carried out before and after each impression was completed to look for evidence of pile-up which invalidates the Oliver and Pharr approach¹² and fracture which affects the validity of the extrapolation approach for coating properties.

III. RESULTS AND DISCUSSION

A. Characterisation of Coatings

Ion beam analysis was undertaken using a 4MeV helium beam at two different angles of incidence to facilitate fitting of the spectra to obtain coating composition from backscattering profiles (Figure 2). For coatings deposited on glass at both deposition temperatures stoichiometric Al₂O₃ coatings were produced with no carbon or hydrogen contamination. Thus the self-limiting ALD reactions had gone to completion during deposition. The thickness determined from a fracture section using scanning electron microscopy was identical to that determined by ellipsometry on silicon (within experimental error). Coatings deposited on PET at 150°C were close to stoichiometric but with some carbon (possibly originating from the PET substrate) and less oxygen whereas at 80°C contained somewhat less aluminium than would be expected from stoichiometry (Table 1) with the balance being made up of oxygen, carbon and hydrogen. According to ion beam analysis the coatings on PET were ~20% thicker than on glass or had lower

density when deposited at 80°C – the latter is most likely to be the case based on the mechanical results in the following section.

The roughness of the coated samples determined by AFM in a 10 micron square region (which is comparable to the size of the deformation around the largest indents tested here) is very low ($<1\text{nm}$) and does not change appreciably after coating for glass and silicon. The roughness of the ALD alumina-coated PET samples does, however, increase by a factor of two. This is due to the effects of residual stress in the coating. The thermal expansion coefficient of the PET substrate is about four times that of the alumina coating. At the end of the deposition cycle the coating and substrate are in thermal and mechanical equilibrium and the cooling of the system to room temperature generates a compressive stress in the coating due to thermal expansion mismatch. This stress is maintained in the coatings on the hard, stiff substrates, but can be reduced by buckling of the coating on the more compliant PET to form a wavy surface. The wavelength of such buckles is much greater than $10\mu\text{m}$ and thus it does not affect the indentation measurements but does contribute to the increase in roughness measured. Long wavelength surface undulations can be seen on the surface but there is no evidence for coating detachment or through-thickness cracking in the coating prior to indentation testing (either by AFM or scans of the surface with the indentation tip in the Hysitron prior to performing each indentation test).

B. Nanoindentation response

Figure 3 shows typical nanoindentation load-displacement curves for the ALD alumina deposited on glass and PET at the two deposition temperatures when compared to the uncoated substrate. Curves have been chosen so that the contact depth is less than 10% of the coating thickness so that substrate effects are minimised. In both cases at the fixed maximum displacement the curves from the coatings deposited at 150°C reach the highest peak load followed by the coatings deposited at 80°C and the substrate has the lowest

peak load. This implies that the hardness and/or stiffness of the ALD coating is greater than that of the substrate as expected and that properties improve as the deposition temperature increases.

The variation of hardness and contact modulus with contact depth for soda-lime glass is shown in Figure 4. Extrapolated coating properties are given in Table 3. To ensure that a valid extrapolation is used it is necessary to remove all data points where elastic behaviour is observed (coincident loading and unloading curve). Also, as can be seen in Figure 4a, at very low loads the hardness increases from a low value and then stabilises; this represents the elastic-plastic transition and these data points should also be ignored in the extrapolation process. The hardness of the glass substrate is lower than the ALD alumina deposited at 150°C but higher than that of the coating deposited at 80°C (Fig 4a) whereas the contact modulus of ALD alumina is always higher than that of soda-lime glass and increases with deposition temperature. In all cases there is a slight increase in hardness above ~40nm contact depth which is not present in the data obtained on fused silica calibration samples at the same contact depth. This is attributed to a softened surface layer on the glass substrate prior to coating which arose due to the chemical changes to the surface (leaching) which occurred during long term storage of the uncoated materials – the hardness stabilizes at much larger contact depths. The indent geometry is well-defined at both deposition temperatures and there is no evidence for pile-up (Figure 5) so the quality of the data expected to be good. Since both the coating and substrate are amorphous the extent of any indentation size effects is likely to be limited and will not affect the analysis^{13, 14}.

ALD alumina coatings deposited on silicon showed very similar extrapolated properties to those on glass as might be expected from the fact that it is a stiff substrate with a similar surface composition.

For the PET substrate there is an increase in hardness with deposition temperature (Figure 6a) as expected but the contact modulus is much lower than that measured on the glass substrate and there is no real difference between the deposition temperatures (Figure 6b). The AFM images of indents show poorly defined impressions and evidence of picture-frame and radial cracking (Figure 7). Given this and the hardness data it is likely that coating fracture started when the contact depth reached around 20nm and the substrate dominates the measured mechanical properties when the contact depth is greater than 30nm. Using the extrapolation method with coatings on PET produces reasonable values for coating hardness but seriously underestimates the contact modulus because of the large elastic deformation of the substrate.

C. Discussion

The properties of ALD alumina on soda-lime glass and silicon are very similar which means that the results determined here can be compared with previous data for coatings on silicon. The contact modulus values are broadly comparable to what has been reported previously (between 160 and 220GPa^{1-4, 16}) whereas the hardness is lower than usually reported (typically 10-12GPa¹⁻⁴) except in the recent publication by Miller et al¹⁶ where the reported hardness of 6.67GPa is within the same as measured here within experimental error.

For both soda-lime glass and silicon the surface initially exposed to TMA is hydrated silicon oxide and the chemical reactions which occur in each ALD cycle will be very similar depending on surface OH groups. For this reason it is not surprising that the thickness of ALD alumina on silicon and soda-lime glass is also almost identical. However, the mechanism of coating deposition on PET will be very different. When TMA is initially let into the ALD chamber there is no surface OH with which it can react and yet a film is deposited. It has been suggested that during ALD alumina deposition on polymers the TMA is adsorbed onto the polymer surface and absorbed into the near surface region and is not pumped away before the water is introduced. Thus reaction initially takes place at the surface and within the polymer substrate and an external coating gradually forms in subsequent ALD cycles¹⁵. The composition of the ALD alumina on PET deposited at 80°C would fit with such a model - it suggests that the coating contains regions of hydrated alumina and PET. Such a graded layer would also tend to improve coating adhesion which may explain why through-thickness fracture of the ALD alumina on PET did not result in interfacial detachment in this study.

Although it is possible to get measurements which appear valid for the ALD alumina coatings on stiff substrates from the data here there remains the question about whether the absolute values of hardness and contact modulus determined are correct. Figure 8 compares the literature data for the contact modulus of ALD alumina as a function of deposition temperature. This data was obtained from thicker coatings and was validated by other measurement methods^{1-4, 16}. The data measured in this study is consistent with the other work and shows a smooth trend, increasing with deposition temperature. The values of contact modulus measured in all cases are consistent with the

values of elastic modulus determined for amorphous alumina of different densities¹⁷.

Several workers have shown that the density of ALD alumina increases with deposition temperature [e.g. ¹⁸] so this result is entirely as expected.

The deposition rate of ALD alumina on all substrates has been shown to increase when the deposition temperature is less than 100°C since water can condense on the substrate surface and layer by layer growth is no longer maintained. Under such conditions it is not surprising that a lower density amorphous alumina is produced with lower stiffness as observed here.

The accuracy of the extrapolation method depends on the accuracy of the contact modulus and hardness data in the extrapolation range of contact depth. When testing bulk materials with well calibrated tips there is often a contact depth below which the hardness or contact modulus is no longer constant which defines the boundary where the measured data is no longer accurate. The reasons for this variation from constant behavior are often complex including the transition from elastic to plastic deformation, indentation size effects and the accuracy of the calibration of the tip when going from the pyramidal region of the indenter to its spherical cap. In the measurements taken here indentation size effects related to plasticity are not significant as the coatings and substrates are amorphous but may have contributed to some of the higher hardness values measured for coatings on silicon in the literature. The transition from elastic to plastic deformation which leads to a rapid increase in hardness at low contact depth can also be taken into consideration by excluding low contact depth data. However, the accuracy of the data obtained when the spherical indenter cap dominates the indentation behavior will always be an issue when testing very thin coatings. It is critical that the data used in the extrapolation contains enough points obtained after the spherical cap depth is exceeded if a good value is to be obtained; in this study about 50% of the data points used for extrapolation came from beyond the spherical cap which is adequate for generating good data.

The low hardness of ALD alumina on PET is most likely due to its composition but the low measured contact modulus is mostly due to the low stiffness of the PET substrate. A simple model for the variation of contact modulus with contact depth for a coating/substrate system based on a truncated cone of load support beneath the coating¹⁹ can be used to assess this. In this model

$$E = \frac{P}{2a_0(\partial_c + \partial_s)} \quad (4)$$

Where P is the indentation load and a_0 the radius of the contact circle which is related to the contact depth. The displacements in the coating and substrate under the indenter are given by

$$\partial_c = \frac{P}{\pi E_c} \left[\frac{1}{a_0 \tan \alpha} - \frac{1}{a_0 \tan \alpha + t_c \tan^2 \alpha} \right] \quad (5)$$

and

$$\partial_s = \frac{P}{\pi E_s} \left[\frac{1}{a_0 \tan \alpha + t_c \tan^2 \alpha} - \frac{1}{a_0 \tan \alpha + (t_c + t_s) \tan^2 \alpha} \right] \quad (6)$$

where E_c and E_s are the Young's Modulus of the coating and substrate, t_c and t_s are the coating and substrate thickness and α is the semiangle of the cone of material which supports the load (measurements on bulk materials give $\alpha=32.48^\circ$). The contact radius can be related to the contact depth, h_c , determined by the Oliver and Pharr method⁶, if the indenter geometry is known. For a Berkovich indenter,

$$h_c = \sqrt{(\pi/k)} a_0 \quad (7)$$

where $k=24.5$. This assumes a perfect tip which is a reasonable assumption for compliant substrates when deformations are large as here.

Taking the extrapolated contact modulus of the ALD alumina on soda-lime glass and predicting the behaviour of the ALD alumina on glass and PET using equation (4) we get an excellent match with experimental data (Figure 8). Thus the results are dominated by the elasticity of the substrate and are relatively insensitive to the coating properties.

IV. SUMMARY AND CONCLUSIONS

This study has demonstrated that reasonable mechanical properties for 150nm ALD alumina coatings can be obtained provided that the coating is deposited on a hard, stiff substrate. When a compliant substrate, such as PET, is used it is not possible to collect sufficient data for extrapolation to give a reliable measurement of the contact modulus of the coating but reasonable hardness values are obtained. Modelling is necessary to extract elastic properties of the coating. The mechanical properties of ALD alumina depend on deposition temperature with increasingly open, low density coatings produced at low temperature having a lower elastic modulus and hardness. Coatings deposited on different substrates in the same deposition run can have a different composition and thickness depending on the details of the deposition mechanism. If mechanical design calculations are to be undertaken for devices containing ALD layers it will be important to measure the properties of the coatings deposited under relevant conditions rather than rely on literature data if the deposition temperature is low and the substrate is compliant.

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Figure Captions

Figure 1. Extrapolation of contact modulus data for 80°C ALD alumina on soda-lime glass to zero depth in order to assess the properties of coating and substrate.

Figure 2. Typical RBS results for 80°C ALD alumina on PET. The experimental data was fitted to obtain composition information and the quality of the fit is good.

Figure 3: Nanoindentation load-displacement curves for ALD alumina deposited onto (a) glass and (b) PET at different deposition temperatures compared to results for the uncoated substrate.

Figure 4. Variation of (a) hardness and (b) contact modulus for ALD alumina on soda-lime glass.

Figure 5. AFM images of 100nm maximum displacement indentations in ALD alumina on soda-lime glass.

Figure 6. Variation of (a) hardness and (b) contact modulus for ALD alumina on PET.

Figure 7. AFM images of 100nm maximum displacement indentations in ALD alumina on PET.

Figure 8. Variation of contact modulus with deposition temperature for ALD alumina.

Figure 9. Predicted contact modulus for ALD alumina on PET based on extrapolated data for ALD alumina on soda-lime glass.

Tables

Table 1: Composition of ALD alumina coatings from ion beam analysis

Coating	Al (atom%)	O (atom%)	C (atom%)	H (atom%)
150°C ALD alumina on glass	40	60	0	0
80°C ALD alumina on glass	40	60	0	0
150°C ALD alumina on PET	40	55	5	0
80°C ALD alumina on PET	13	30	23	34

Table 2: Roughness of uncoated and coated substrates determined by AFM.

Substrate	Deposition temperature (°C)	Ra (nm)
Silicon	No coating	0.13±0.05
	80	0.15±0.06
	150	0.17±0.05
Glass	No coating	0.40±0.09
	80	0.52±0.15
	150	0.41±0.08
PET	No coating	0.18±0.11
	80	0.27±0.15
	150	0.38±0.17

Table 3: Extrapolated coating hardness and contact modulus values.

Substrate	Deposition Temp (°C)	Alumina Hardness (GPa)	Alumina Contact Modulus (GPa)
Silicon	80	4.83±0.09	125±6
	150	6.44±0.12	172±9
Glass	80	4.85±0.10	121±5
	150	6.34±0.15	162±8
PET	80	2.05±0.09	36.2±1.8
	150	2.46±0.08	43.7±0.7

Figures

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(a)

(b)

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