



ELSEVIER

Contents lists available at [SciVerse ScienceDirect](http://www.sciencedirect.com)

International Journal of Adhesion & Adhesives

journal homepage: www.elsevier.com/locate/ijadhadhInternational Journal of
Adhesion &
Adhesives

Evaluation of contamination of ceramic surfaces and its effect on epoxy bleed

O. Williams^{a,*}, D.P. Webb^a, C. Liu^a, P. Firth^b^a Mechanical and Manufacturing Engineering, Loughborough University, LE11 3TU, UK^b Oclaro, Westfield Business Park, Long Road, Paignton, Devon TQ4 7AU, UK

ARTICLE INFO

Article history:

Accepted 21 February 2011

Available online 12 October 2011

Keywords:

Epoxy/epoxides

Ceramics

X-ray photoelectron spectroscopy

Contact angles

ABSTRACT

A degree of surface contamination has been found to be beneficial for assembly quality of optoelectronics because it reduces the surface free energy of the ceramic substrates, therefore inhibits bleed of the epoxy adhesives used to assemble components to them. This study aimed to examine the implications for process control of current industrial practice where the control of ceramic surface free energy is not considered. This has been achieved by identifying and characterising the potential sources of the contamination found on ceramic sleds, which had passed through the optoelectronic supply chain, so that the variation in chemical composition and the degree of contamination could be determined.

Two types of ceramic substrates, aluminium oxide and aluminium nitride were cleaned by plasma, then stored in commercial polymer waffle packs used for transportation and a variety of storage atmospheres for one month. XPS measurements to characterize the surface chemistry were subsequently carried out following the storage to identify the composition of contamination that had built up. Contact angle and bleed distance measurements were also made to quantify the effect of the contamination on the wetting properties of the contaminated surfaces.

It was found that the composition of the contamination was not directly associated with the storage method or environment, but the quantity was. The highest degree of contamination occurred on samples stored using the industrial standard method of containment in polymer waffle packs with paper and polyethylene anti-static inserts, higher even than storage in open air. The major source of the contamination in this case was probably from the inserts, with a much smaller contribution from the waffle pack. The levels of contamination built up in such case produced apparent surface free energies only slightly lower than 30 mJ/m², the threshold for acceptable levels of bleed to occur during the assembly process. This has indicated that if storage were to be used as a method of controlling epoxy bleed, it is likely that episodes of epoxy bleed would occur in a random manner on the production line, due to variation in the sample storage conditions and tendency to adsorb contaminants.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

The adsorption of contaminants onto high surface free energy aluminium oxide and aluminium nitride optical bench materials can be detrimental to the quality and reliability of optoelectronic modules assembled from them using adhesives. Such assemblies are frequently hermetically sealed, after being baked for 12 h at 150 °C, to remove all traces of water and other contaminants, which could affect the in service performance. During the production of the ceramic sleds a number of cleaning and firing stages are used to maintain cleanliness. However, in some instances the contamination can be beneficial for assembly quality because of the effect on surface wetting. In particular, epoxy bleed has been seen to be inhibited by carbon based contamination associated with a lowering

of surface free energy, which is one driving force of the phenomenon [1]. Epoxy bleed is the separation of the liquid adhesive components from the bulk material and their spread across a substrate surface. Allowing for such spread reduces the packing density of components that can be achieved on a sled surface. Excessive bleed, which occurs unpredictably, can also interfere with subsequent assembly processes such as wire bonding.

The origin of contamination can be from a number of sources, namely: atmosphere, handling, surface treatments and outgassing from storage media [2]. Contamination arising from handling and surface treatments can be easily controlled or avoided, but that which originates from storage media or the atmosphere is difficult to manage. Although contamination can have the desirable effect of inhibiting epoxy bleed, depending on this contamination for assembly quality is questionable. One reason for this is the random nature of its composition and occurrence as seen in a previous study [1], investigating the epoxy behaviour on commercially prepared ceramics sourced from different suppliers with varied

* Corresponding author.

E-mail address: OwainW86@gmail.com (O. Williams).

surface preparations. While it was concluded that contamination of the ceramic surfaces in the as-received state did not detrimentally affect bond strength regardless of surface finish, it was also found that the level of contamination present was not sufficient to stop epoxy bleed in all cases, namely on the samples with high surface roughness. Uncontrolled levels of surface contamination may also have undesirable effects on other steps in optoelectronic module assembly, such as the application and adhesion of conductive metal tracks.

However, relying on contamination for epoxy bleed control is effectively the current industry practice, even if process engineers do not currently recognise this. The aim of this study was to examine further the implications of the current industry practice for the quality control of optoelectronic assembly by identifying potential sources for the contamination found on ceramic sleds passing through the optoelectronic supply chain, and determining the degree of variation in chemical composition and quantity of such contamination. It was hypothesised that samples fresh from suppliers will not have built up sufficient contamination to reduce the surface free energy to a degree such that bleed will not occur. In the study, optoelectronic quality ceramic sleds were cleaned and then stored in various control environments and environments representative of the supply chain. A subsidiary aim was to examine the effectiveness of various cleaning methods at removing the contamination thus built up, as a precursor to engineered methods of controlling surface free energy.


2. Materials and methods

Sample preparation was undertaken at Loughborough University, UK. Aluminium oxide and aluminium nitride tiles of 1 mm thickness were diced into $5 \times 14 \text{ mm}^2$ samples using a CO_2 laser. The diced samples were then put into deionised water and treated with ultrasonics for 5 min to remove any residue from the laser cutting process. Following the sonic treatment the samples were rinsed in IPA to begin organics removal and to aid drying. Samples were then dried in a flow of air at 60°C for 10 min. When the samples were dry they underwent one minute of treatment in a 300 W oxygen RF (13.56 MHz) plasma at a flow rate of 100 sccm. Oxygen plasma was used for its effectiveness at organic molecule oxidation [3,4]; as organic molecules had been seen to form the majority of surface contamination in previous work [1]. Following plasma treatment the samples were transferred to the storage media. These were closed in aluminium foil as a control, and polymer waffle packs with inserts as typically used in the industry for transport and storage. To reduce particulate contamination in the short time between plasma cleaning and sealing of the storage media the process was undertaken in a class ten thousand (ISO 7) clean room.

The storage conditions studied were: storage in a clean room in an optoelectronic module assembly site in Shenzhen, China with uncontrolled temperature, storage in a nitrogen cabinet in the assembly site with uncontrolled temperature, an environmental chamber controlled at 100% humidity at $25 \pm 1^\circ\text{C}$ at Loughborough University, and storage in a class ten thousand (ISO 7) clean room at Loughborough University. All samples were stored for thirty days before being analysed with XPS, contact angle measurements and bleed distance measurements. During shipping to Shenzhen for storage, and back to Loughborough for analysis, all polymer waffle packs were sealed in polythene bags to protect them from the uncontrolled conditions of transit. The waffle packs used in the study were made of polycarbonate with added carbon powder and were manufactured by Entegris. They were supplied with polythene and lint free paper inserts, intended to

Table 1

Possible present bond types with their respective binding energies where BE is binding energy in electron volts (eV) with reference to the $\text{C}1s$ peak at 285.00 eV.

Carbon bond type	BE
$\text{C}1s$	285.00
$\text{C}-\text{O}-\text{C}$	286.45
$\text{N}-\text{C}$	285.94
$\text{N}=\text{C}$	285.96
Epoxide 	287.02
$\text{C}-\text{OH}$	286.55
$\text{O}-\text{C}-\text{O}$	287.93

protect the samples, and which were used for storage, unless otherwise noted.

The post storage cleaning methods subsequently implemented were: oxygen plasma cleaning, a combination of solvent cleaning and oxygen plasma cleaning, and firing. The plasma cleaning method used had the same parameters, 300 W oxygen RF (13.56 MHz) plasma at a flow rate of 100 sccm, as the initial cleaning of the surfaces before storage. Plasma cleaning was done for 1 min and 5 min. For the combined solvent with plasma cleaning method the samples underwent an IPA wash and air dry followed by 1 min of plasma treatment. The firing was performed using a sample dryer with an air flow at 400°C . Samples were exposed to the air flow for 5 min. Following cleaning, samples were not returned to waffle packs but were sealed into aluminium foil pouches until further analysis took place within 24 h.

Samples were analysed using XPS, contact angle measurements and bleed distance measurements. XPS wide scans of three regions on the surface of each stored sample were recorded. A narrow band scan around the carbon binding energy area was also made for each sample. All XPS analyses were performed with a Kratos AXIS ULTRA with an Al X-ray source and a $300 \times 700 \mu\text{m}^2$ analysis area. Peaks were fitted to the narrow band spectra according to the data in Table 1, which was populated from the literature [5–9]. Apparent surface free energy estimations were made from contact angle measurements. The test liquids were diiodomethane and water and the estimation of the surface free energy was made using the Owens Wendt method. Nine measurements at different positions on each sample surface were made for each estimation.

Bleed distance was measured using scanning electron microscopy. It was taken to be the maximum distance measured from the edge of the adhesive spot to the edge of the bleed along a line normal to the tangent to the edge of the adhesive spot. The bleed was distinguished from the adhesive bulk by contrast difference in the image.

3. Results and discussion

3.1. The effects of storage

The degree of adsorption of organic contamination onto the ceramic surfaces stored under different conditions was consistent with that observed on the commercial samples studied previously [1]. It can therefore be concluded that its presence is not due to bad practice or equipment related contamination, but that the contamination has another source.

Table 2 gives the relative atomic percentages of all of the elements detected on the stored sample surfaces. The detection of any element with a presence higher than 0.1 relative atomic

Table 2

Relative atomic composition percentage of stored ceramics, mean values of three measurements made with XPS. Foil means stored in aluminium foil. All other samples stored in waffle packs.

Storage conditions/material	No.	O	Al	Si	C	N	F	Na	K	Ca
Foil AlN	1	53.7	19.5	4.5	12.6	4.4	4.4	0.3	0.6	0.2
Nitrogen AlN (China)	2	45.6	18.0	2.9	26.0	3.1	1.7	1.4	1.1	0.2
100% humidity 25 °C AlN	3	44.7	15.5	3.5	29.2	3.3	1.1	0.8	1.7	0.3
Clean room AlN (China)	4	44.8	18.6	2.6	27.9	4.1	1.5	0.5	0.4	0.2
Foil Al ₂ O ₃	5	46.4	19.1	4.1	19.2	0.4	8.0	1.8	1.5	0.2
Nitrogen Al ₂ O ₃ (China)	6	44.2	17.6	5.3	29.7	0.6	1.2	0.6	0.8	0.2
100% humidity 25 °C Al ₂ O ₃	7	40.0	12.5	9.4	36.4	0.5	1.2	0.6	0.1	0.1
Clean room Al ₂ O ₃ (China)	8	45.4	17.8	4.6	29.4	0.5	1.1	0.8	0.6	0.2

percentage was recorded. As expected, the presence of group 1 and 2 metals was associated with the purity of the as received ceramics. However, the appearance of silicon on the surfaces was unexpected, and no specific source can be identified. Mould release agents from the injected moulded waffle packs could explain its presence on the samples stored in waffle packs, but not those stored in the aluminium foil. Fluorine was also detected, most significantly on the samples stored in aluminium foil. However, the abundance of fluorine did not correlate with the surface free energy measurements and so was not considered further. The presence of the aluminium, oxygen and nitrogen can all be attributed to the ceramic materials. AlN clearly shows higher nitrogen content on the surfaces than the alumina, which was to be expected. Both of the ceramics show a high degree of oxygen on the surfaces. This supports the hypothesis of a presence of an aluminium oxide layer on the aluminium nitride surfaces. This also explains the lower than expected nitrogen value for the AlN, which should be in a 1:1 ratio to the aluminium signal, should no other aluminium compound be present. The oxygen is also present at a higher concentration than the 2:3 aluminium to oxygen ratio that would be expected for Al₂O₃. This indicates that some oxygen signal can be partially attributed to the organic contamination.

A statistical measure, the Pearson product-moment correlation coefficient r , was used as a measure of the dependence of elemental abundance upon the prevalence of other elements. The sample correlation coefficient was calculated using the following equation for pairs of elements in Table 3:

$$r(X,Y) = \frac{\sum(x-\bar{x})(y-\bar{y})}{\sqrt{\sum(x-\bar{x})^2 \sum(y-\bar{y})^2}} \quad (1)$$

The element combinations, which gave an absolute value higher than 0.7, which denotes some element of correlation, are shown in Table 3. The correlation between the substances of low relative percentage is not considered in this table. This is because the quantification resolution of the XPS equipment is $\sim 1\%$ so correlations between elements of relative presence $< 1\%$ cannot be considered significant.

The data analysis technique proved to be moderately useful for highlighting potential correlations between elements but offers no interpretation as to why the correlations identified exist. However, an important conclusion can be drawn from the negative correlations between carbon and oxygen, and carbon and aluminium seen on both ceramics. This suggests that the contaminants may have an inhibiting effect on the signal from the oxide, possibly due to the masking effect of an overlying layer of contamination on the signal from the ceramics' aluminium oxide surface layer, and is consistent with the low aluminium to oxygen ratios noted previously. The data also suggests that the silicon is not associated with the carbon, since the AlN shows a negative

Table 3

Relative atomic composition percentage correlations for AlN and Al₂O₃ on stored samples.

AlN			Al ₂ O ₃		
Element 1	Element 2	r	Element 1	Element 2	r
F	O	1.00	Al	O	0.99
F	C	-1.00	Si	O	0.99
C	O	-1.00	Si	Al	0.99
Si	O	0.89	F	C	0.88
Si	C	-0.85	C	O	-0.87
Al	C	-0.71	Al	C	-0.86
C	N	-0.70	Si	C	0.83
			N	F	-0.83

correlation while, on the contrary, aluminium oxide shows a positive correlation.

Fig. 1 shows the variation of carbon loading with respect to storage method. The unstored parts are ones, which had been subjected to plasma cleaning only and analysed within 24 h. Interestingly, the aluminium foil wrapped samples show little or no contamination build up compared to the other storage methods. Aluminium foil is widely regarded to be effective at protecting samples from airborne contaminants [10]. This could be for a number of reasons including its manufacturing method including a corona discharge cleaning stage, it being tightly rolled excluding air between the layers, and aluminium foil having a greater affinity for contamination build up than the ceramics stored in it.

It may be surmised from Fig. 1 that a source for the contamination is the waffle packs used for storage, and as this source was not present in the aluminium foil the ceramics did not absorb the same degree of contamination. The waffle pack stored samples are mostly within the range of 25–30% relative carbon coverage. The high mean value of 37% for the aluminium oxide stored under high humidity is due to a single high result of 49% from the three measurements, the other two being within the 25–30% range. This suggests that the distribution of contamination on the surfaces is not completely uniform.

Fig. 2 shows the peaks fitted to the XPS narrow scan spectrum from sample 1 (Foil stored AlN) whilst Fig. 3 shows the peaks fitted to the spectrum from sample 8 (Al₂O₃ stored in a clean room). It can be seen that although the relative carbon contents of the two surfaces, as listed in Table 2 are very different, the narrow band spectra, which provide the best method of identifying the bond types present, are very similar suggesting similar functional groups. It can also be seen from the figures that the counts per second (CPS) value is over double the value for sample 8 when compared to sample 1. This is due to the higher percentage presence of carbon on sample 8 (29.4 at%) than sample 1

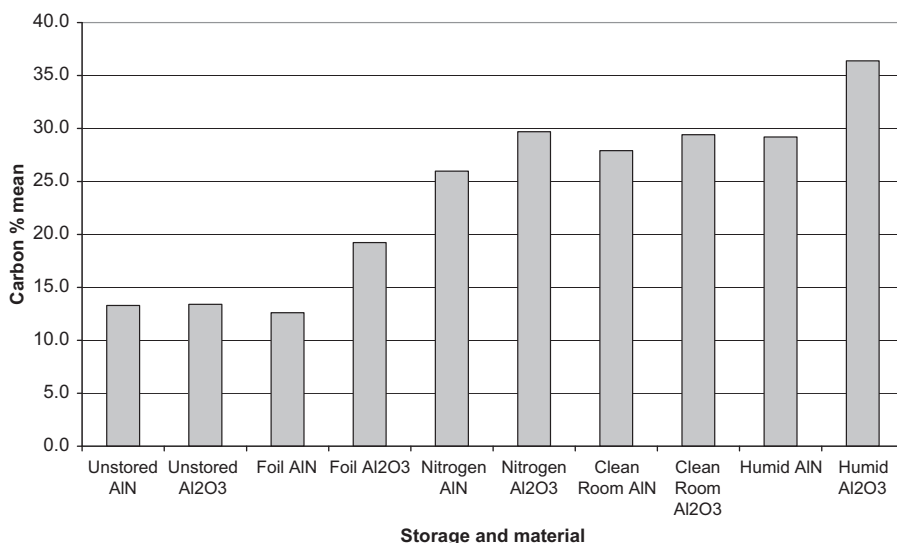


Fig. 1. Relative carbon atomic percentage for all stored samples showing the effect of storage on the build up of contamination following the initial clean.

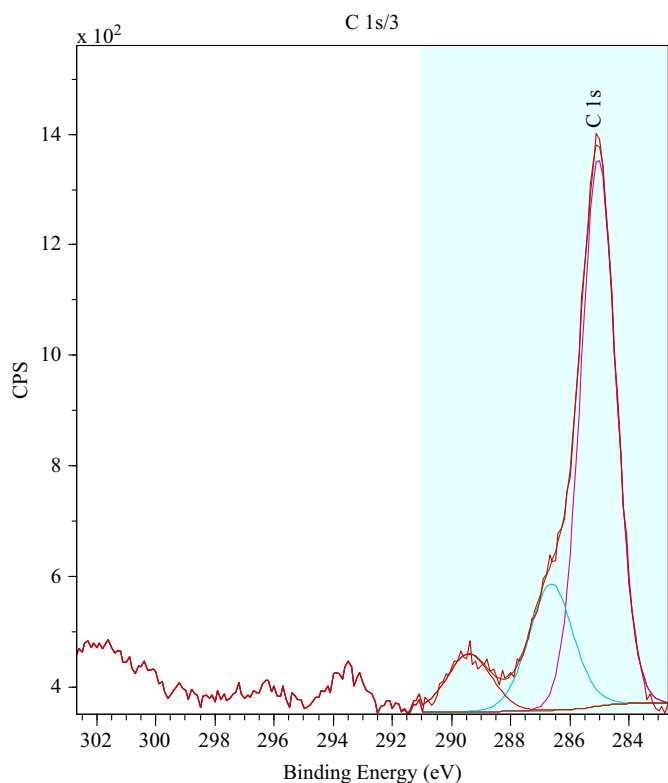


Fig. 2. Narrow scan spectra of carbon peak for sample 1 with fitted contributory peaks, corrected to 285 eV. Where the purple line is the C1s contribution, the green line the C–O contribution and the red line the COOR contribution, and the brown line the fitting summation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

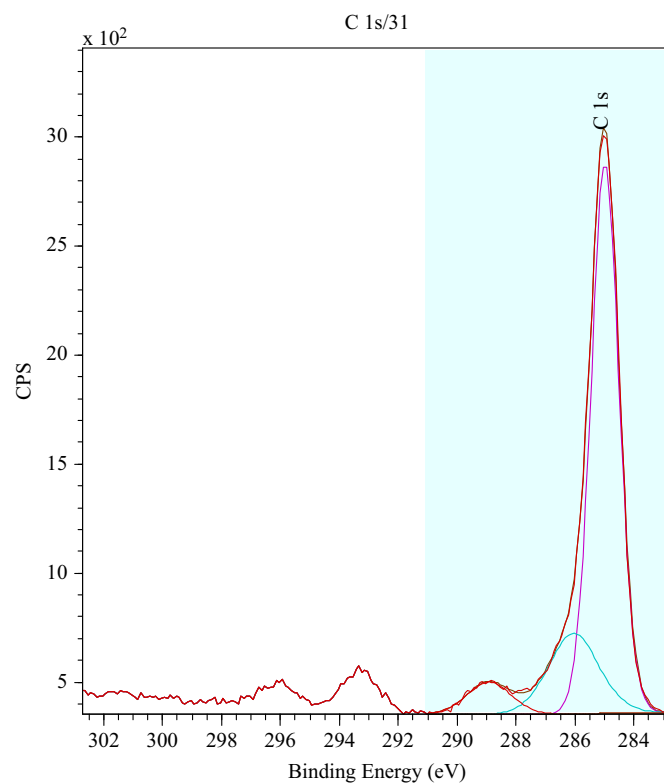


Fig. 3. Narrow scan spectra of carbon peaks for sample 8, corrected to 285.00 eV. Line colours as for Fig. 2.

Table 4

Relative bond type percentages from fits to narrow band XPS spectra of all stored samples.

Sample	No.	C1s	C–O	O–C=O
Foil AlN	1	70.15	20.46	9.39
Nitrogen AlN	2	78.64	15.94	5.42
Humid AlN	3	82.19	11.90	5.91
Clean room AlN	4	76.00	20.09	3.91
Foil Al ₂ O ₃	5	78.28	15.51	6.21
Nitrogen Al ₂ O ₃	6	70.47	24.45	5.08
Humid Al ₂ O ₃	7	75.17	24.83	0.00
Clean room Al ₂ O ₃	8	73.52	19.48	7.00

(12.6 at%). However it should also be noted that the ratios of the peak magnitudes are almost identical, again suggesting that the chemical nature of the contamination is very similar.

The ratios of the bond type abundances from the narrow band fits for all the stored sample conditions are shown in Table 4. It can be seen from Table 4 that 70–80% of the carbon bonds are C–C and C–H bonds (i.e. C1s bonds), 10–25% are C–O bonds and the remainder are carboxylic acid COOR bonds. The data suggests that the composition of the organic contamination was principally carbon, oxygen and hydrogen as all peaks could be attributed to

these elements. The nature of the contamination suggests that it either came from the atmosphere and not the polycarbonate waffle packs, or that the compositions of atmospheric adventitious carbon is similar to that, which might be outgassed from polymers. Reasons for this are the similarity of the distribution of bond types of the foil stored samples and the waffle pack stored samples, as noted in the comparison of samples 1 and 8. Further evidence to suggest that the polycarbonate has not outgassed monomers or oligomers onto the surface is the lack of evidence of a carbonate group, i.e. a C=O peak at 287.8 eV is not seen in any of the XPS spectra, which would be expected from polycarbonate. There is still the possibility of the source of the contamination being other constituents of the waffle packs, such as outgassed polymer additives and leached carbon filler.

The results of contact angle measurements on the storage samples are summarised in Table 5. The table shows a correlation between effective surface free energy and carbon percentage.

Table 5
Contact angle and surface free energy data of stored samples. CA=contact angle (°), SE=surface free energy (mJ/m²).

Sample	Carbon %	Water CA	Diiodomethane CA	SE
Foil AlN	12.6	55.3	54.6	45.34
Foil Al ₂ O ₃	19.2	53.8	48.2	50.65
Nitrogen AlN	26.0	104.7	65.6	25.9
Nitrogen Al ₂ O ₃	29.7	100.3	62.7	27.05
Clean room AlN	27.9	102.3	72.1	21.44
Humid AlN	29.2	104.2	69.9	22.99

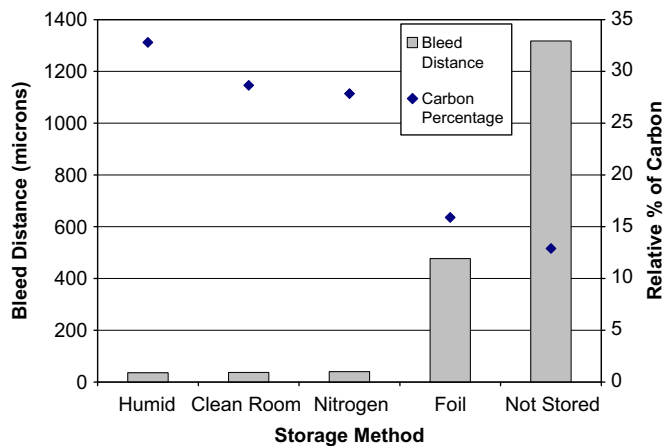


Fig. 4. Epoxy bleed distance of the 930-4 epoxy compared to relative atomic carbon percentage on stored and not stored AlN surfaces.

Table 6
Relative atomic composition percentage of cleaned ceramic surfaces, mean values of three measurements made with XPS. The storage conditions for samples prior to cleaning are specified in the text. Samples 17–20 had not undergone storage.

Cleaning method/material	No.	O	Al	Si	C	N	F	Na	K	Ca
1 min oxygen plasma AlN	9	52.1	16.7	5.8	15.2	5.2	4.6	0.2	0.0	0.3
5 min oxygen plasma AlN	10	54.7	18.0	5.8	13.3	4.4	3.6	0.2	0.0	0.2
IPA+oxygen plasma AlN	11	54.8	18.7	5.9	12.2	4.5	3.6	0.2	0.0	0.0
Fired AlN	12	53.9	19.6	4.1	15.4	5.4	0.0	0.7	0.7	0.3
1 min oxygen plasma Al ₂ O ₃	13	56.6	19.7	5.4	12.7	1.0	4.6	0.1	0.0	0.2
5 min oxygen plasma Al ₂ O ₃	14	56.8	20.3	5.6	12.0	0.5	3.7	0.5	0.6	0.4
IPA+1 min oxygen plasma Al ₂ O ₃	15	56.4	19.8	6.0	12.9	0.9	3.2	0.4	0.2	0.2
Fired Al ₂ O ₃	16	54.6	22.1	3.5	16.3	0.3	0.5	1.2	1.3	0.2
1 min oxygen plasma Al ₂ O ₃	17	55.6	19.7	5.5	13.4	0.9	4.8	0.0	0.1	0.1
5 min oxygen plasma Al ₂ O ₃	18	57.6	20.4	5.9	12.5	0.7	2.9	0.0	0.0	0.0
IPA+1 min oxygen plasma Al ₂ O ₃	19	57.5	20.4	6.0	12.1	0.8	3.3	0.0	0.0	0.0
Firing Al ₂ O ₃	20	57.1	21.2	5.1	14.9	0.3	0.5	0.4	0.5	0.2

Correlation was not seen between the effective surface free energy and the bond type abundances found in the carbon high resolution narrow band scan. However, correlation was seen between the relative atomic percentage of oxygen and carbon and the effective surface energies ($r=0.99$ and -1.00 , respectively). The negative correlation between the surface energies and the relative atomic percentage of carbon was consistent with data acquired from commercial samples [1].

Fig. 4 shows the results of the maximum epoxy bleed distance measurements on the aluminium nitride stored and not stored samples. A correlation between the amount of organic contamination present and the bleed distance can be clearly seen. A similar correlation was also observed on aluminium oxide. As the bleed distance for all the waffle pack stored samples is negligible at $<50 \mu\text{m}$, it seems that the storage of samples in waffle packs for one month is sufficient to stop the bleed occurring to levels significant for manufacture. However ceramic sleds may experience cleaning steps during manufacture, which could reduce the bleed resistance.

3.2. The effects of cleaning

A number of samples stored under all conditions were cleaned using the methods described previously. Samples 9 and 10 were previously stored in the nitrogen cabinet in Shenzhen, samples 11–13 and 16 were stored in the clean room in Shenzhen, samples 14 and 15 were stored at 25°C and 100% humidity and 16–20 were not stored. Table 6 and Fig. 5 show the relative atomic

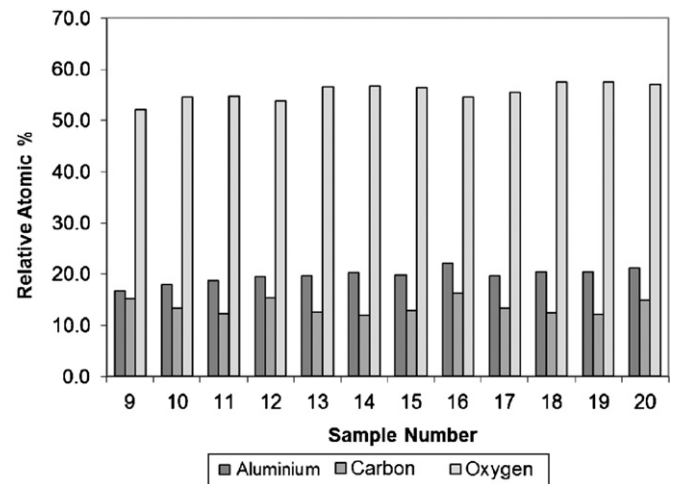


Fig. 5. Relative atomic percentages of aluminium, carbon and oxygen on all AlN and Al₂O₃ surfaces cleaned post storage.

composition percentages obtained from XPS spectra from the cleaned samples.

It can be seen by comparing Table 6 and Fig. 5 to Table 2 that the carbon percentage has been significantly reduced by all of the forms of cleaning. However, some carbon still remains suggesting that either the contamination is re-adsorbing before XPS measurement or that it was not completely removed. Table 6 also shows the marginally increased effectiveness of the plasma cleaning when the process time is increased from 1 min to 5 min. This suggests that all of the carbon was not removed under cleaning, and hence that the processes are not completely effective. However, for a five-fold increase in process time only 1–2 at% extra carbon is removed, which is a negligible difference from the point of view of wetting and epoxy bleed. It should be noted that all cleaned samples showed an effective surface free energy slightly in excess of 70 mJ/m² and an epoxy bleed distance consistent with this surface free energy and the sample roughnesses. Samples 17–20 had not undergone any storage and were prepared freshly for the XPS study for purposes of comparison. It can be seen that there is very little difference between the composition of the stored and unstored cleaned samples, suggesting that the extra contamination which arose from the storage conditions was completely removed by cleaning.

Oxygen plasma cleaning also appeared to be effective at removing fluorine contamination. It can be seen in Table 6 that the fluorine detected is further reduced by around 1 at% by the extended processing time. As the silicon signal is unchanged after cleaning, it confirms that the silicon is not associated with any other of the elements detected, and so it could be a bulk constituent.

All samples show an increased signal from the aluminium following cleaning, by an average 10%, corresponding to an average increased signal of 2.5 at%, while the reduction in the quantity of carbon is accompanied by an increased detection of oxygen. An associated change in bond type distribution is seen in the narrow band carbon spectra shown in Figs. 6 and 7. As shown

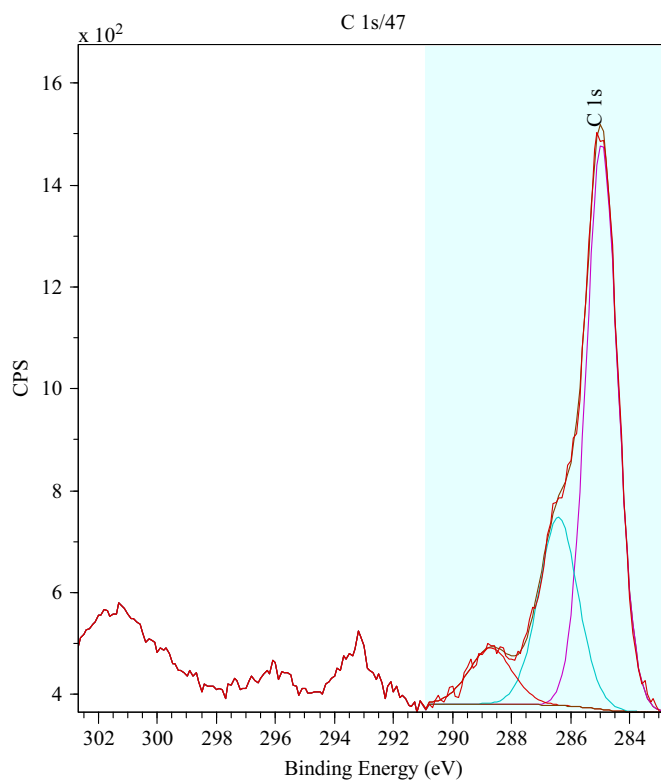


Fig. 7. Narrow scan spectra of carbon peaks for sample 12 (fired AlN which had been stored in a waffle pack in a clean room), corrected to 285.00 eV. Peaks outside the area highlighted in blue can be attributed to trace potassium. Line colours as for Fig. 2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 7

Relative bond type percentages from XPS narrow spectra fitting for cleaned samples.

Sample	No.	C1s	C–O	O–C=O
1 min oxygen plasma AlN	9	70.1	23.1	6.8
5 min oxygen plasma AlN	10	61.7	28.9	9.4
IPA + oxygen plasma AlN	11	63.7	29.8	6.6
Firing AlN	12	64.5	26.8	8.7
1 min oxygen plasma Al ₂ O ₃	13	59.2	31.8	9.1
5 min oxygen plasma Al ₂ O ₃	14	58.9	36.5	4.6
IPA + 1 min oxygen plasma Al ₂ O ₃	15	69.0	23.9	7.1
Fired Al ₂ O ₃	16	64.4	25.1	10.5
1 min oxygen plasma Al ₂ O ₃	17	62.7	32.4	5.0
5 min oxygen plasma Al ₂ O ₃	18	57.8	30.9	11.4
IPA + 1 min oxygen plasma Al ₂ O ₃	19	51.9	39.9	8.2
Firing Al ₂ O ₃	20	59.5	30.0	10.5

in Table 7 the quantities of carbon–oxygen bonds have increased dramatically. In fact the relative percentage of C–O bonds has increased from 10–25% in Table 4 to 23–40%. This result indicates that the plasma has probably oxidised the organic contamination. A further conclusion is that the contamination, which is present after cleaning is not entirely due to re-adsorption. More evidence for this is that the contaminant composition following cleaning is not similar to the aluminium foil stored (uncleaned) samples, but is more heavily oxidised. This suggests that the composition of the contamination on a ceramic surface stored in aluminium foil changes over time, but does not increase by a large amount. It should be noted the cleaned samples were stored in aluminium foil before analysis.

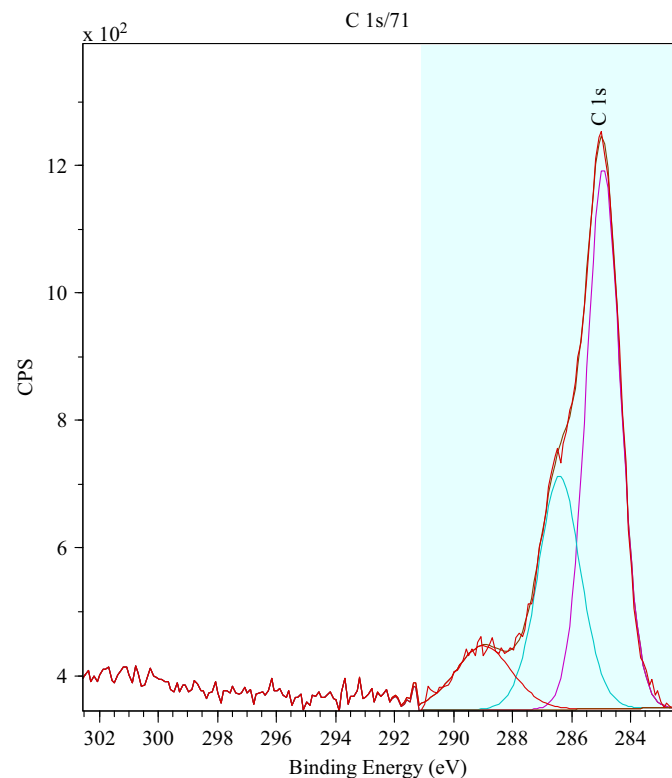


Fig. 6. Narrow scan spectra of carbon peaks for sample 18 (unstored 5 min oxygen plasma cleaned Al₂O₃), corrected to 285.00 eV. Line colours as for Fig. 2.

The relative percentages of carbon bond types were multiplied by the total carbon signal to get figures for atomic surface percentages of bond types. For the three AlN samples 2, 9 and 10, (nitrogen stored AlN, 1 min and 5 min plasma cleaned AlN following nitrogen storage), the total carbon atomic percentages were 26, 15.2 and 13.3, respectively, which showed a decrease in carbon on the surface due to cleaning. There was an accompanying slight decrease in the total presence of each of the C–O and COOR groups, and a much greater decrease in the C–C/C–H percentage. This could be attributed to oxidation of the carbon contaminants (although one would expect an increase in their prevalence), or it could be due to the increased resistance of the COOR groups to removal due to chemisorption [11], or a resistance to further oxidation. This pattern of changes in bond type surface percentages was seen repeatedly, when samples of the same ceramic type and stored under the same conditions are compared following different cleaning methods. For example samples 8, 13 and 16 show the same pattern (clean room UK stored alumina: uncleaned, following 1 min plasma, following firing), as do samples 7, 14 and 15 (humidity chamber stored alumina: uncleaned, following 5 min plasma, following solvent/plasma). The hypothesis of remnant carbon, which is more difficult to remove due to the combined effects of chemisorption and high oxygen content, as opposed to the physical adsorption of saturated hydrocarbons, could explain the incomplete removal of carbon contamination by plasma cleaning. However, due to the affinity of the ceramics for adventitious carbon, re-adsorption is almost certainly responsible for some of the detected presence following cleaning.

The effective surface free energy measurements of the cleaned ceramics show a linear correlation to surface carbon content as seen in Table 5 and previous work [1]. In Fig. 8 the data of Table 5 is plotted on a graph of effective surface free energy versus surface carbon content. Extrapolating a least squares linear fit to the data in the figure yields a zero carbon surface free energy for the ceramics of approximately 50 mJ/m². Fig. 8 also suggests that the surface free energy does not vary linearly with carbon concentration at low carbon concentration. In fact the surface free energy of pure aluminium nitride is not 50 mJ/m² as the extrapolated best fit line suggests, but estimates in the literature for both AlN and alumina lie in the range of 1 J/m², which is significantly higher [12,13].

The surface free energy estimations for the plasma cleaned samples suggest that the oxidation of the organic contamination or higher relative prevalence of oxygen containing species reduces its hydrophobicity. This can be seen in Fig. 8 where the effective surface free energy of the point representing the

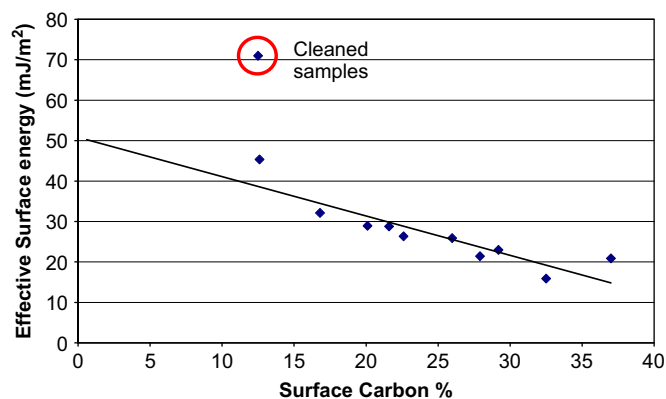


Fig. 8. Carbon % compared to effective surface free energy for storage contaminated samples (data in Table v). Also shown is the mean value for all post storage cleaned samples. The line is a linear fit to the contaminated sample data.

Table 8
Relative atomic composition percentage correlation coefficients (*r*) for AlN and Al₂O₃ on stored and cleaned samples.

Element 1	Element 2	<i>r</i> Pre-clean	<i>r</i> Post-clean
AlN			
F	O	1.00	−0.23
F	C	−1.00	−0.41
C	O	−1.00	−0.77
Si	O	0.89	0.03
Si	C	−0.85	−0.62
Al	C	−0.71	−0.10
C	N	−0.70	0.92
Al₂O₃			
Al	O	0.99	−0.40
Si	O	0.99	0.79
Si	Al	0.99	−0.82
F	C	0.88	−0.78
C	O	−0.87	−0.70
Al	C	−0.86	0.80
Si	C	0.83	−0.90
N	F	−0.83	0.89

averaged cleaned sample data lies far above that for the trendline for the contaminated samples (71 mJ/m² as against 40 mJ/m² extrapolated value). This effect agrees with data in the literature on the effects of plasma treatment on the surface free energy of polymer surfaces [14].

Table 8 compares values of correlation coefficient for pairs of elements before the samples were cleaned and following cleaning. It can be seen that the correlation coefficient retained the same sign and was still significant (absolute value > 0.7) only for C–O on both materials, and for Si–O in Al₂O₃. The reduction in the absolute value of *r* for carbon and oxygen post-clean is probably due to the extra ceramic surface exposed and the oxygen associated with this. Correlation was not found between effective surface free energy and the presence of any of the non-bulk elements, excluding carbon. There was also no correlation found between the percentage distribution of the carbon bond types, which showed variation, and the effective surface free energy, which was consistently > 70 mJ/m². This shows the effectiveness of the cleaning methods to achieve a uniform surface quality in terms of effective surface free energy, from different surface composition starting points.

3.3. The rate and source of contamination

The contamination rate and source was examined experimentally by storing samples at Loughborough and conducting measurements after 24 h, 48 h, 1 week, 2 weeks and 4 weeks. The storage conditions investigated were:

1. The atmosphere in a clean room (Air)
2. Waffle packs with supplied inserts in a clean room (polythene and lint free paper), (Waf/Ins)
3. Waffle packs with no inserts in a clean room, (Waf)
4. Waffle pack sealed in aluminium foil in a clean room, (Waf/Foil)
5. Waffle pack containing both inserts, wrapped in aluminium foil, in a clean room, (Waf/Foil/Ins)
6. Sealed aluminium foil pouch in a clean room (Foil)
7. Waffle pack with only the paper insert, wrapped in aluminium foil, in a clean room (Waf/Foil/Paper).

The sample numbers corresponding to each condition are listed in Table 9, and the variations in apparent surface free energy with time for each sample are shown in the graph in Fig. 9.

Table 9

Storage conditions for samples in rate of contamination study. Waf=waffle pack, ins=lint free paper and polyethylene insert, foil=aluminium foil storage, air=storage in open air, and paper=storage with just lint free paper insert.

Storage condition	Material	Sample number
Air	AlN	21
Air	Al ₂ O ₃	22
Waf/ins	Al ₂ O ₃	23
Waf/ins	AlN	24
Waf	Al ₂ O ₃	25
Waf	AlN	26
Waf/foil	Al ₂ O ₃	27
Waf/foil	AlN	28
Waf/foil/ins	Al ₂ O ₃	29
Waf/foil/ins	AlN	30
Foil	AlN	31
Waf/foil/paper	AlN	32
Waf/foil/paper	Al ₂ O ₃	33

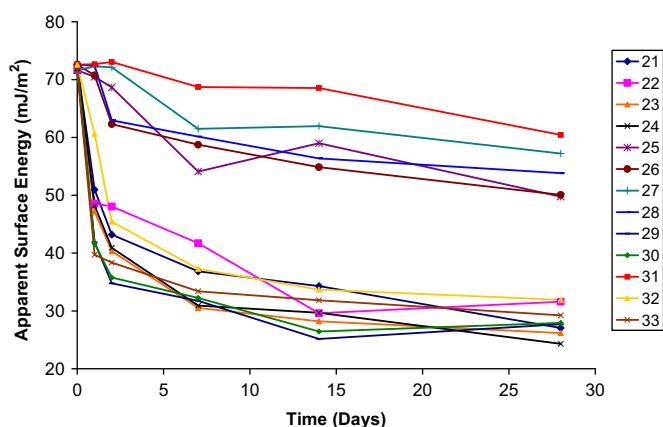


Fig. 9. Graph showing the change in apparent surface free energy compared to time spent stored under various conditions. The samples fall into two clear groups, Samples 25–28 and 31 with relatively high surface energies, and the remaining samples.

One of the more obvious observations to be made from the data is the relative effectiveness of waffle packs without inserts to maintain cleanliness. It can be seen in Fig. 9 that the samples fall into two clear groups, samples 25–28 and 31 with relatively high surface energies, and the remaining samples. The high surface free energy group consists of the samples contained in waffle packs without inserts, either foil wrapped or not foil wrapped, and the foil only wrapped sample, 31, which was still the best performer.

The question of the source of the majority of contaminants to be expected for samples stored by the industry standard method appears to be answered by the results for samples 27–30, which were all samples stored in waffle packs wrapped in foil, where 27 and 28 were stored without inserts and exhibit a much smaller change in surface free energy than 29 and 30, which were stored with both polymer and lint free paper inserts. As it has already been shown that the foil largely excludes external contaminant over the time scale of the experiment, the polymer insert and lint free paper therefore appear to be the source of the majority of contaminants.

To separate the effects of the two different insert types, lint free paper inserts only were used with waffle packs and aluminium foil for samples 32 and 33. It was observed that the contamination rate and magnitude were less with only paper than when polyethylene inserts are included, but more than the rate and magnitudes observed with waffle packs only or packing

with aluminium foil. It can therefore be concluded that both the lint free paper inserts and polyethylene inserts are responsible for outgassing and the subsequent adsorption onto the ceramic surfaces.

The results for samples 25–28 and sample 31 also highlight the waffle pack itself as a source of contaminants, even if at a far lower level than the inserts. It can be concluded that the waffle pack probably outgases to an extent, because sample 31 (aluminium foil, AlN) always exhibits a lower contact angle than the aluminium wrapped foil samples contained in a waffle pack, i.e.; since the foil is effective at reducing the flux of contamination onto the sample surface from external sources as has been demonstrated, the source of contamination on the surface of samples contained in the foil wrapped plain waffle packs (27—Waf/Foil Al₂O₃, 28—Waf/Foil AlN) must be the waffle pack. In addition, the fact that the contact angles for the samples in the non foil-wrapped plain waffle packs (25—Waf Al₂O₃, 26—Waf AlN) are consistently slightly higher than those for the foil wrapped packs, implies that the aluminium foil either prevents an external flux of contaminants reaching the sample surface, or that the foil preferentially adsorbs some of the flux from the waffle pack, or both.

Fig. 9 shows that the industry method of storing the samples in waffle packs with polymer and lint free paper inserts is equivalent to leaving samples open to the atmosphere of a class 10,000 clean room, in terms of organic contamination. For example Sample 22 (Air Al₂O₃) exhibits a consistently lower surface free energy than the sample 23 (Waf/Ins Al₂O₃). The same was seen with AlN, samples 21 (Air AlN) and 24 (Waf/Ins AlN). Fig. 9 also shows that the adsorption rates of the samples, which adsorbed adventitious carbon at a lower rate (25–28 and 31) over the time were relatively constant during the measurement periods. It is likely that the surface loadings of contamination would eventually reach that seen on the highly contaminated samples. By contrast the contamination loadings on the highly contaminated samples 21–27, 29–30 and 32–33, levelled off after an initial high adsorption rate period, suggesting the equilibrium status of adsorption rate matching desorption rate was reached after 28 days.

Interestingly, the samples which showed the highest degree of contamination, as inferred from contact angles, were those stored by the industry recommended method, with lint free paper and polyethylene inserts. The apparent surface free energies reached by these samples, 26.19 mJ/m² and 24.31 mJ/m² for aluminium oxide and aluminium nitride, respectively, lie only slightly inside the surface free energy threshold value [1] (30 mJ/m²) below which the degree of epoxy bleed is considered to be acceptable. Thus if storage were to be used as a method of controlling epoxy bleed, it is likely that episodes of epoxy bleed would occur at random on the production line, due to variation in the sample storage conditions and tendency to adsorb contaminants. Sources of variation include varying partial pressure of contaminants and temperature of storage conditions, and heterogeneity of surface properties over samples and between batches affecting tendency to adsorb contaminants.

4. Conclusions

The detailed examination of the surfaces of optoelectronics grade ceramic substrates (i.e. AlN and Al₂O₃) under the various storage conditions and the effects of the level of contaminations on the epoxy bleed has been carried out, based on the results obtained the following conclusions can be drawn:

1. The composition of the contamination on the ceramic surfaces cleaned and then stored for 28 days under conditions representative of the industrial environments, and control

conditions, was not directly associated with their storage methods or environments, but that the level of contamination was. In particular it was found that the highest degree of contamination occurred on the samples stored using the industrial standard method of containment in polymer waffle packs with paper and polyethylene anti-static inserts, higher even than storage in open air. The source of the majority of the contamination in this case was found to be probably the inserts, with a much smaller contribution from the waffle pack. The use of aluminium foil by itself for storage can reduce the degree of contamination significantly, but not prevent build up entirely. The use of polymer waffle packs without inserts was also found to reduce contamination build-up significantly over open air storage, although to a lesser degree than with foil. A high degree of bleed was seen in both samples cleaned but not stored, and samples cleaned after storage, showing the effects of storage contamination are easily reversed.

2. The carbon content on the surfaces was found to be a good predictor of the degree of bleed. A moderate degree of contamination, about 30 at% of carbon, reduces bleed to an insignificant level. However, the levels of contamination built up in the worst case, of storage in waffle packs with inserts, produced apparent surface free energies only slightly lower than the 30 mJ/m² threshold for acceptable levels of bleed. Therefore, if storage were to be used as a method of controlling epoxy bleed, it is likely that episodes of epoxy bleed would occur at random on the production line, due to variation in the sample storage conditions and tendency to adsorb contaminants. Longer storage would probably not improve the situations, since the change rate of surface free energy observed from the heavily contaminated samples after 28 days was insignificant. To control epoxy bleed due to the variations of surface contamination two strategies are suggested. One is to use contact angle measurement as a screening procedure by giving a quick estimate of the surface free energy, and therefore the level of contaminations. The other is to put the ceramic surfaces into a known state, by routinely cleaning on receipt followed by a

suitable treatment to reduce the surface free energy to a stable level that inhibits bleed.

References

- [1] Williams O, Liu C, Webb DP, Firth P. Epoxy adhesive behaviour on ceramic surfaces in commercial optoelectronic assemblies. *Int J Adhes Adhes*, ISSN: 0143-7496 2010;30(4):225–35.
- [2] Saga Koichiro, Hattori Takeshi. Identification and removal of trace organic contamination on silicon wafers stored in plastic boxes. *J Electrochem Soc* 1996;143:3279.
- [3] Tezuka M, Yajima T. Oxidation of aromatic hydrocarbons with oxygen in a radiofrequency plasma. *Plasma Chem Plasma Process* 1996;16:329–40.
- [4] Tezuka M, Yajima T. Oxidation of cycloalkanes in a radiofrequency plasma. *Bull Chem Soc Jpn* 1991.
- [5] Briggs D David. *Surface analysis of polymers by XPS and static SIMS*. Cambridge: Cambridge University Press; 1998.
- [6] Zhang B, Wei B, Sullivan D, Gotts HE. A systematic study of a-CN_x overcoat film for proximity recording. *IEEE Trans Magn* 1997;33:3109–11.
- [7] Zhu Q, Money SL, Russell AE, Thomas KM. Determination of the fate of nitrogen functionality in carbonaceous materials during pyrolysis and combustion using X-ray absorption near edge structure spectroscopy. *Langmuir* 1997;13:2149–57.
- [8] Bhattacharyya A, Roy Rita, Sen SK, Sen Suchitra, Chakraborty AK, Bhattacharyya TK. X-ray photoelectron spectroscopic studies of conducting polyaniline, poly bisphenol A carbonate and electrochemically synthesized composite of the two. *Vacuum* 1998;49(4):253–6.
- [9] Awaja Firas, Pigram Paul J. Surface molecular characterisation of different epoxy resin composites subjected to UV accelerated degradation using XPS and ToF-SIMS. *Polym Degradation Stability*, ISSN: 0141-3910 2009;94(4):651–8, doi:10.1016/j.polymdegradstab.2009.01.001.
- [10] Shelton LR. Field guide for collecting samples for analysis of volatile organic compounds in stream water of the National Water-Quality Assessment Program: US Geological Survey Open-File Report 97-401; 1997, 14 p.
- [11] Karaman ME, Antelmi DA, Pashley RM. The production of stable hydrophobic surfaces by the adsorption of hydrocarbon and fluorocarbon carboxylic acids onto alumina substrates. *Colloids Surf A* 2001;182:285–98.
- [12] Asai H, Iwase N, Suga T. Influence of ceramic surface treatment on peel-off strength between aluminum nitride and epoxy-modified polyaminobisamide adhesive. *IEEE Trans Adv Packag* 2001;24(1):104–12.
- [13] Guzman-Castillo ML, Bokhimi X, Rodriguez-Hernandez A, Toledo-Antonio A, Hernandez-Beltran F, Fripiat JJ. The surface energy of quasi-amorphous [gamma] alumina calculated from the temperature of the [gamma]->[alpha] transition. *Journal of Non-Crystalline Solids* 2003;329(1–3):53–6. In: Proceedings of the 7th international workshop on non-crystalline solids, 1 November 2003, ISSN 0022-3093, doi:10.1016/j.jnoncrsol.2003.08.012.
- [14] Mittal KL. *Polymer surface modification: relevance to adhesion*. Utrecht: VSP; 1996.