

Application note

Surface Energy determination on thin wires using picolitre drops

The surface energies of a tinned and a pure copper wire have been determined measuring contact angles with various liquids using the optical contact angle measuring and contour analysis system OCA 200 in combination with the picolitre dosing system PDDS. With this system it is possible to determine the surface energy directly on the thin wires, which are just a few 100 μm in diameter, since optimizing the shape and minimizing the volume of the picolitre drops allows to reliably measure contact angles even on smallest surfaces.



Fig. 1: picolitre dosing system PDDS

Background

Digitalization is one of the biggest transformations the industrial world has been facing since the end of the 20th century. Estimations show that in 2007 around 94 % of the technological information capacity worldwide has been digital, compared to only 3 % in 1993 [1]. The steady growth of digitalized sectors and their future security stand and fall with the continuous optimization of computers, processors and power electronics. This optimization is going along with miniaturization of all electronic parts.

In view of the processing of these miniaturized parts (such as gluing of metal parts to polymer- or semiconductor-based circuit boards, soldering or bonding metal wires to semiconductors, or laser welding of wires) a crucial step for securing the efficiency and long-time stability of the final product is the characterization of the individual surfaces with regard to cleanliness/lack of contaminations and compatibility to each other.

Contact angle measurements with various test liquids and the determination of the substrate's surface energy according to the OWRK method [2-4] are widely used to check surface properties and get an insight into the cleanliness of a surface.

For metals one can state, in general, the higher the surface energy the cleaner the surface or the less oily and fatty contaminations are still attached to the surface.

Standard contact angle measurements are performed with liquid drops of microlitre volume, which means that for a reliable measurement surface areas of up to a few centimetres are required. To measure on, e.g., smallest bond positions or wires of only a few 100 μm in diameter much smaller drops, of only picolitre volume, are needed.

The picolitre dosing system PDDS by DataPhysics Instruments (Fig. 1) allows to generate single drops of a few 10 pL; hence, in combination with the optical contact angle measuring and contour analysis system OCA 200 (Fig. 2) it is the optimal device to determine surface energies of smallest parts like wires or bond positions on circuit boards. For the said measurements it is crucial, in order to obtain reliable results, to minimize the volume of the dispensed drop and to optimise and stabilise its shape.

Thus, in the application note at hand we demonstrate how to proceed to generate optimal, reliable drops with the PDDS as we present the determination of the surface energy of two copper wires.



Fig. 2: DataPhysics Instruments optical contact angle measuring and contour analysis system OCA

Experiment

Examined Samples

The surface energies of a pure and a tinned copper wire were to be determined. The diameter of the pure copper wire was $D = 190 \mu\text{m}$ and the one of the tinned copper wire $D = 250 \mu\text{m}$.

The aim of the experiments was to see if tinning the copper minimizes the contamination with oily and fatty films which often hinders a good and long-time stable bonding on circuit boards, or, in other words, to see which wire has a higher surface energy indicating a cleaner surface and, presumably, a better comparability in further bonding processes. Both wires have been characterized untreated in any way.

Minimization/Optimization of the drop size

To ensure proper contact angle measurement with unhindered wetting, the picolitre dosing system PDDS had to be controlled such that it generated test liquid drops with wetting areas smaller than half the diameter of the wires.

The drops are generated by acoustic impulses, where the dispensing pulse parameters, amplitude, width and frequency, can be adjusted using the analysis and control software SCA of the device (see Fig. 3).

The possibility of generating drops of a few picolitres comes along with the complexity of very individual dispensing parameters for each liquid to be used. Thus, the parameters are optimized for each liquid according to the following procedure:

1. Cartridges of various nozzle diameters ($D = 50 \mu\text{m}$, $70 \mu\text{m}$, $100 \mu\text{m}$) are available for use with the PDDS. In order to dispense drops of the smallest possible volume it is advisable to always use the cartridge with the smallest possible nozzle. Whether a selected nozzle diameter will work with the respective liquid can easily be tested directly by filling the cartridge of choice:
If it is possible to fill the cartridge by sucking in the liquid through the small nozzle then dispensing will, in almost all cases, also be possible. Filling is not possible if the liquid possesses a too high viscosity. This reflects that the minimal possible volume for drop dispensing strongly depends on the viscosity of the liquid.

As a rule of thumb, liquids with viscosities close to the one of water can normally be dispensed with the smallest available nozzle diameter ($D = 50 \mu\text{m}$) while liquids of higher viscosity ($>10 \text{ mPa s}$) usually require bigger nozzle diameters. An opportune proceeding is to start with the biggest nozzle diameter and decrease it step by step until filling the cartridge through the nozzle is no longer possible.

2. When the cartridge is filled with the liquid it is convenient to apply a slight negative pressure (Pressure Sensor Threshold) which prevents leakage and also the formation of a liquid discus at the nozzle, which is adverse in terms of stable dispensing.
3. When the cartridge filled with the liquid is placed in the PDDS dispenser head one starts, in order to optimize and minimize a single drop, to at first dispense either single drops, or drops in continuous mode (with frequencies of 200 Hz or lower), with the highest possible amplitude (100) and biggest width (100). It is generally useful to use a homogeneous, flat and non-absorbing surface as substrate to allow for a good observation of the dispensed drop.
 - a. If no drops can be dispensed one should check that no liquid discus is formed at the end of the nozzle. If so the liquid discus has to be removed, either dispensing continuously for a while, or using a soft tissue. Should the liquid discus form again it is advisable to increase a bit the negative pressure, i.e. increase the pressure sensor threshold (e.g. for diiodomethane the value should be set to 3 - 4 due to the material's relatively high density). If afterwards it is still not possible to dispense drops, not even in continuous mode, then a bigger nozzle diameter must be used.
 - b. If no stable individual drops but drops accompanied by satellite drops are dispensed one can decrease the pulse amplitude and pulse width in single steps down to around 80. Experience shows that in most cases stable individual drops can be achieved for the first time with parameter values in the range between 100 and 80. The difference between the amplitude and the width value should be kept between 0 and 15.
 - c. If after adjusting the pulse amplitude and width according to step (b) there are still

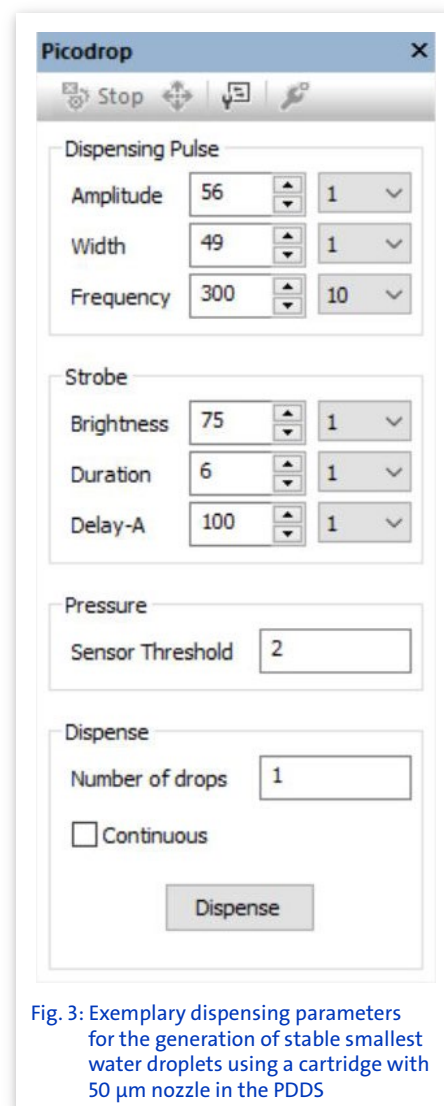


Fig. 3: Exemplary dispensing parameters for the generation of stable smallest water droplets using a cartridge with $50 \mu\text{m}$ nozzle in the PDDS

satellite drops observable, or the single drop is still too large, it can be given a try to further decrease the amplitude and pulse values until stable single drops are observed. Since sometimes the drop visible on the substrate consists of two dispensed drops which have combined during the time of flight, lowering the parameters might erase one of the drops and thus minimize the drop on the substrate. However, if the approach to reduce the dispensing pulse parameters fails to result in sufficiently small drops (note that below certain values dispensing is no longer possible) then the only way out is to switch to a smaller nozzle diameter, or go for another liquid.

Liquid	Nozzle [μm]	Amplitude	Width	Frequency	Pressure	Drop volume [pL]
Water	50	56	49	300	2	61
Diiodomethane	70	82	78	200	4	120
DMSO	100	100	85	200	2	81
Ethylene Glycol	100	53	89	200	2	130
Ethylene Glycol	50	93	88	300	2	65

Table 1: Exemplary dispensing parameters

Table 1 shows some exemplary dispensing parameters for standard test liquids, which have been set up according to the method described above. Since reproducible dispensing is dependent on parameters like temperature, filling height of the cartridge and many more, all information within this table is subject to change and shall only be taken as indication.

Another possibility to optimize drops during the flight is to make use of the strobing function. The explanation of this method though is beyond the scope of this application note.

Test liquids

DataPhysics Instruments recommends using diiodomethane, ethylene glycol, thiodiglycol and water as standard test liquids for the determination of the surface energy. However, the viscosity of thiodiglycol is too high for dispensing drops with the PDDS.

It is thus recommended to work with benzylic alcohol or DMSO instead, whose polar to disperse ratios of the surface tension are similar to that of thiodiglycol. Further alternative liquids can be found, e.g., in the ISO standard 19433:2017 [5]. Note that in any case it is important to make sure that the selected test liquids do not chemically react with the substrate to be analysed.

Results

For surface energy determination of the two wires contact angles have been measured with diiodomethane, benzylic alcohol and ethylene glycol. An exemplary image of benzylic alcohol drops on the pure copper wire is shown in Fig. 4. The picture has been recorded within the SCA software which was also used to evaluate the contact angles.

On each wire at least three drops per test liquid have been dispensed with the PDDS and the mean contact angles have been calculated (cp. Table 2).

Obviously the contact angles on the tinned copper wire are smaller than those on the pure copper wire.

Table 3: Surface Energy (SE) of the wires together with the polar (SE^p) and dispersive (SE^d) components

Sample	SE [mN/m]	SE ^d [mN/m]	SE ^p [mN/m]
Pure copper wire	29.7	29.1	0.6
Tinned copper wire	36.0	34.8	1.2

Using the contact angle values of table 2, the surface energy (SE) of both wires has been calculated according to the OWRK method [2-4]. Table 3 lists the respective results together with the polar (SE^p) and dispersive (SE^d) components of the SE.

The described experiment revealed that the surface energy of the examined tinned copper wire with 36.0mN/m is much higher than the surface energy of the pure copper wire with 29.7 mN/m. The polar component of the SE is very low for both wires.

Since higher surface energies usually implicate cleaner surfaces, which are beneficial for further processing like wire bonding, the tinned copper wire appears favourable against the pure copper wire with view to ensure long-time stable products.

Summary

The progressive miniaturisation going along with the global digitalisation process of today raises the need for material characterisation of smallest building components, such as wires, bond positions, etc.

Cleanliness of these parts is crucial for ensuring long-time stability and efficiency of the products; hence, the absence of contaminations must be checked carefully to be able to initiate corrective action where needed.

A particularly useful approach is to investigate the wetting behaviour and determine the surface energy of the material. However, carrying out measurements on real samples, which is of course preferable to benchmark tests, is quite a challenge since only tiny areas are available on the components.

The optical contact angle measuring and contour analysis system OCA 200 in combination with the picolitre dosing system PDDS from DataPhysics Instruments offers a specific solution. It allows dispensing drops which, by optimization of the dispens-

ing parameters, can be minimised down to a few 10 pL. These drops can be used to measure contact angles even on smallest substrates with surfaces of down to only a few 10 µm.

This has been shown in the application note at hand by the example of a pure and a tinned copper wire whose surface energies were determined using the OCA 200 together with the PDDS.

References

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- [2] Kaelble, H.; J. Adhesion: Dispersion-Polar Surface Tension Properties of Organic Solids.; 1970, 2; S. 66-81.
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- [4] Rabel, W.: Einige Aspekte der Benetzungstheorie und ihre Anwendung auf die Untersuchung und Veränderung der Oberflächeneigenschaften von Polymeren.; Farbe und Lack 77; 1971, 10; S. 997-1005.
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Table 2: Mean contact angles of the 3 test liquids on the examined wires

Sample	Mean contact angle [°]		
	Diiodomethane	Benzylic alcohol	Ethylene glycol
Pure copper wire	58.4	52.2	71.5
Tinned copper wire	48.7	34.7	60.8

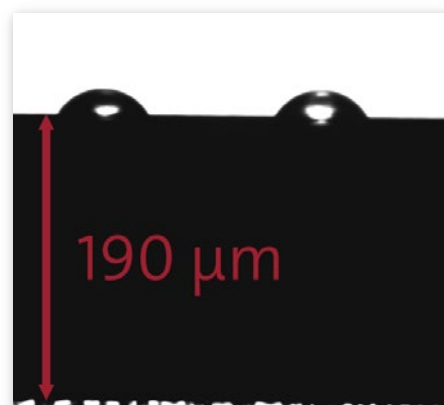


Fig. 4: Drops of benzylic alcohol dispensed on the pure copper wire with a diameter of 190 µm, which gives a reference for the drop size