DESIGN NOTE

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Calibration of an optical fluorescence method for film thickness measurement

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Abstract
We describe the calibration of a technique allowing quantitative
measurements of industrial coatings with thicknesses as small as 10–20 nm.
Wax films doped with fluorescent rhodamine dye have been deposited by an
electrospray method onto an optically flat surface of aluminium-coated
glass. The films were of 220–450 nm peak thickness, which we measured
with an optical profilometer using laser triangulation. Possession of a set of
films allowing an absolute calibration of the fluorescence intensity versus
thickness to be achieved for application in trials of the fluorescence method
for measuring coating thicknesses of 10–20 nm under industrial process
conditions.

(Some figures in this article are in colour only in the electronic version; see www.iop.org)

1. Introduction

We have developed an optical technique for monitoring the
thickness of a very thin wax coating (the *release layer*) during
the manufacture of hot stamping foil [1]. Hot stamping foil,
which is used to print metallic text and images onto packaging,
is a multi-layer structure deposited onto a polymer carrier foil,
typically 12 μm thick. The release layer is a wax coating
approximately 10 nm thick, which allows the carrier to be
cleanly separated from the metallic print left on the product at
the hot stamping stage. Its estimated thickness of 10 nm is a
bulk average derived from the take-up of wax solution on the
coating machine. Our method is based on the measurement
of the fluorescence intensity of a fluorophore, rhodamine 101
dye (R101), incorporated into the coating which allows the
thickness of the release film to be monitored on-line during the
industrial coating process. The ability to monitor the release
thickness during process is necessary in order to improve the
quality control of the final foil product.

Several authors have reported the use of laser-induced
fluorescence to monitor liquid films and solid coatings. The
calibration methods depend on the nature and thickness of
the measurand films. For example, Kimura and Takami [2]
measured relatively thick photoresist coatings (100 μm to
1 mm) by using a stylus scan, whereas Takesue *et al* [3] spin-
coated sample flux and oil films 0.2–4 μm thick onto a silicon
wafer and determined their thicknesses by interferometry
or ellipsometry. Thicknesses of lubricating oil film in the
micrometre range have been calibrated using calibration blocks
with known depth steps [4]. Very thin lubricant films with
dye tracers have been investigated for application to magnetic
hard disks [5], but the thickness of 10 nm was estimated from
absorption of optical energy and the extinction coefficient of
the fluorescent dye, without a separate thickness calibration.

We describe the preparation and thickness measurement
of R101-doped wax films for calibration of the fluorescence
signal for application to results from industrial trials. The
calibration films must be sufficiently thick to be measured by
an independent technique and it is preferable to retain the same
wax and dopant as in the industrial foil release layer to facilitate
comparison of results. It is not practical to use the industrially

produced coatings themselves as calibration samples for two reasons: the release layer is too thin for reliable measurement and is suspected to be locally too non-uniform to allow accurate registration for intercomparison with the fluorescence signal. Thicknesses of transparent dielectric coatings have been measured by phase-stepped white light interferometry [6], but the convergence of the fit to the interferogram becomes unreliable for thicknesses below 50 nm. Hence we have prepared R101-doped wax calibration films with thicknesses of the order of several hundred nanometres on glass substrates. Although interferometric measurement of films of this thickness is possible, we employed a commercial optical profiler instrument to scan the upper film surface and surrounding substrate. Contacting stylus profile methods are clearly undesirable for a soft material such as wax.

If the wax coating of thickness z is doped with a uniform concentration D of fluorophore, resulting in an absorption coefficient BD at the excitation wavelength, and is exposed to an excitation beam of intensity I_0, then the fluorescence power emitted per unit area of the coating is

$$I_F = \phi I_0[1 - \exp(-BDz)] \qquad (1)$$

where ϕ denotes the quantum efficiency of the fluorophore. In the limit of low concentration and small absorption, (1) approximates to

$$I_F = BD\phi I_0 z. \qquad (2)$$

It is convenient to detect the fluorescence signal over a range of wavelengths $\lambda_1 < \lambda < \lambda_2$ chosen to discriminate against background light and to integrate the detected spectrum over a time τ. Hence, for an excitation spot area A, the fluorescence signal will be given by

$$S_F = A\tau \int_{\lambda_1}^{\lambda_2} I_F(\lambda)\, d\lambda = zABD\phi I_0 \tau \qquad (3)$$

that is, the fluorescence response is linear with respect to the film thickness. Laboratory measurements on doped wax solution showed that the fluorescence intensity varied linearly with the integrated amount of dopant excited over a range of five orders of magnitude. Thus internal filtering and quenching effects were negligible at the dopant concentrations used, so the assumptions inherent in equation (3) were justified. The linear dependence of the fluorescence intensity on the relative thickness is shown in figure 1 for sets of wax release coated polymer sample films made with eight different weights of release coat (i.e. area densities), each with five concentrations of dopant. Figure 1 is a relative calibration showing a linear response to a variation in the product of dopant concentration and coating weight from 3×10^{-7} to 1200×10^{-7} g m^{-2}. This is equivalent to a coating thickness range of 0.35 nm to 140 nm at a typical dopant concentration of 0.15% by weight in wax. Calibration measurements on films in the region of a few hundred nanometres thickness should therefore scale linearly to in-process measurements on 10 nm films at the same concentration of dopant.

Hence, having demonstrated the linearity of S_F with thickness z, an absolute calibration was required in order to allow the thickness of the release coat to be established. The aim of the work described here was the fabrication and independent measurement of doped films of known thicknesses.
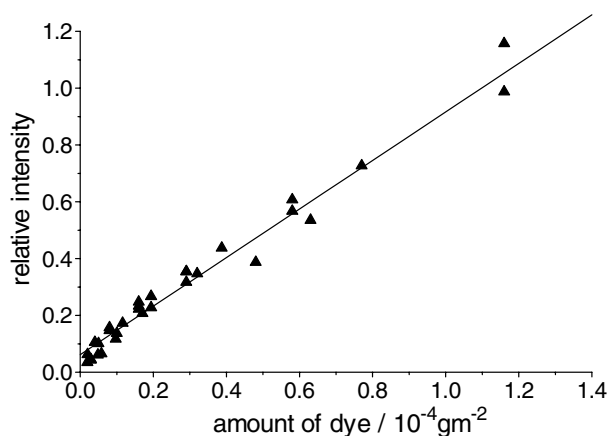

Figure 1. A relative calibration demonstrating the linear dependence of the fluorescence intensity on the integrated amount of dopant for samples of R101-doped wax release coat on a polymer carrier foil (34 points, $R^2 = 0.978$).

2. Preparation of calibration samples

Calibration films of R101-doped release wax were prepared using the electrospray method [7, 8]. In this method a solution is sprayed from a small nozzle, usually a hypodermic needle, held at a potential of several kilovolts relative to a substrate which is earthed. The electrical field promotes the break-up of spray droplets on their exit from the nozzle and assists evaporation of solvent before the coating is formed. This results in effectively dry deposition of the solute onto the target.

A solution in toluene–ethanol of 2.5 g l^{-1} of release wax doped with 0.15% by weight of R101 in wax was sprayed from a 27 gauge hypodermic needle held at a potential of +8.5 kV relative to the substrate; the needle-to-substrate distance was about 50 mm. The substrate was an indium tin oxide (ITO) coated optical flat with a secondary coating of aluminium. The aluminium coating was necessary for successful operation of the laser surface profilometer described below. Although it was possible to produce thin electrosprayed films on an uncoated glass substrate, a conducting substrate was found essential for good uniformity and for the build-up of films of several times 100 nm thickness. By masking and spraying the substrate for increasing time intervals, it was possible to deposit several films of different thicknesses onto the same substrate.

The same R101-doped wax solution was used for the preparation of all calibration samples. Therefore, the accuracy of the dye concentration affects only the comparison between the calibration samples and the doped foil samples. The discrepancy in dye concentration between the two types of sample is estimated to be less than 10%.

Normal variations in ambient temperature exerted to significant influence on the fluorescence intensity of R101-doped wax films. There was no evidence of photobleaching on the timescale of the calibration measurements; doped foil samples exhibited no apparent degradation of the fluorophore after about 12 months.

3. Thickness measurement of calibration samples

The coated slides were measured on a scanning laser surface profilometer (Scantron Proscan 1000) using a reflective laser-
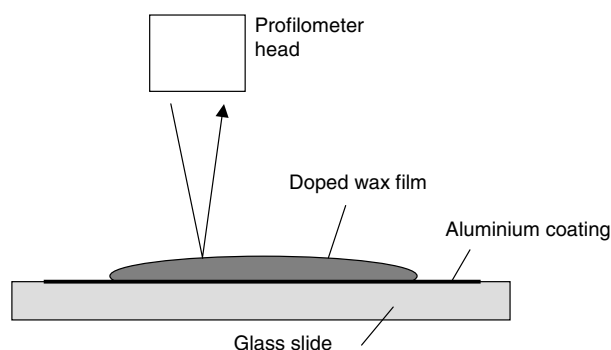
Figure 2. A schematic diagram of a profilometer scan of a calibration slide: the thickness of the wax film is exaggerated for clarity. The upper surface of the aluminium coating is the reference plane for the film thickness measurement.

beam triangulation sensor (Anritsu KL131A). The sensor comprised a class 3B semiconductor laser of wavelength 780 nm and a position sensitive detector. The diameter of the laser spot varied in the range 12–35 μm across the 400 μm measurement range with the minimum value mid-range. The slides were measured at the upper limit of the range in order to maximize the averaging effect of the sensor. A sampling interval of 20 μm was chosen, with each data point representing an average of 64 measurements.

The arrangement for the profilometer scan is shown schematically in figure 2. The aluminium coating on the optical flat resulted in a good reflected profilometer signal and hence a clear definition of the baseline height at the margins of the area of the wax sample. Scans made on substrates without the secondary aluminium coating gave indeterminate results since the triangulation sensor received reflections from both upper and lower surfaces of the substrate. The ITO optical flat substrate was chosen because it offered an improvement in flatness over conventional microscope slides. With film thicknesses of hundreds of nanometres a flatness of at least $\lambda/20$ over the area of the sample was desired. This was difficult to achieve using conventional slides.

Figure 3 shows a two-dimensional thickness scan of a typical wax sample electrosprayed for 4 min. The surface in figure 3 has been levelled by the removal of a least squares mean plane based on the surrounding aluminium surface. The height is also relative to this surface at the border of the wax sample of area approximately 4 mm square. Since the fluorescence measurements represent an average over a spot approximately 2 mm in diameter, for comparison purposes the maps from the profilometer were subjected to a moving average filter. In this instance each data point is the (unweighted) average of all data points within a circle of diameter 2.4 mm centred on that point. Six calibration films were measured using the profilometer to give thickness maps similar to figure 3, with peak values of the area-averaged thickness ranging from 226 to 457 nm, typically 25 nm lower at a distance of 0.5 mm from the peak.

The samples were also investigated using a scanning white light interferometer. These measurements were of limited success in that the transparency of the thinner areas resulted in measurement of the underlying substrate while the thicker areas were measured from the top surface. The resulting combination of high (valid) and low (artefact)

surfaces prevented estimation of the mean film thickness. The general magnitude and distribution of the high points did appear to correspond to that observed with the triangulation sensor and thus provided a limited means for cross checking of the data.

4. Fluorescence measurement of calibration samples

4.1. The reduction of signal due to quenching

Initial laboratory measurements were made using a Spex Fluoromax spectrofluorimeter (Instruments SA), which has a xenon lamp excitation source and a red-sensitive photomultiplier tube detector (Hamamtsu R928P). The fluorescence intensity was measured as a function of the lateral position across the films by mounting the sample on a motorized translation stage and exciting and detecting the fluorescence via optical fibre bundles coupled to the spectrofluorimeter. The spatial resolution, determined by the diameter of the excitation beam, was 2 mm. We made a direct comparison measurement between the fluorescence intensities of two calibration films, measured to be 300 ± 30 and 800 ± 80 nm thick, and a sample of release coat on polyester carrier. The calibration films and the foil sample were doped at the same concentration of 0.15% dye by weight in wax. The observed fluorescence intensities indicated the thickness of the release coat to be 200 ± 30 nm on the basis of a linear comparison with the calibration signals. This was far in excess of the thickness of 10–20 nm estimated on the basis of the rate of deposition of release coat solution in manufacture. Further investigation using foils prepared with and without aluminium layers revealed that the fluorescence intensity of R101-doped release wax films deposited on an aluminium substrate is reduced by a factor of 10 ± 2 relative to that for films on a dielectric substrate, such as the polyester carrier. The quenching of fluorescent molecules on conducting substrates is well known; it is due to transfer of electronic energy from the excited molecule to the conducting layer [9]. Hence a factor of 10 ± 2 is required in the conversion from the fluorescence signal from the calibration samples to that measured during an industrial process.

4.2. Calibration measurements

The calibration samples were measured using the optical probe designed for use in the industrial trials [1]. The doped samples were excited with a frequency-doubled, CW Nd:YAG laser (532 nm wavelength) giving a spot nominally of 1 mm diameter on the sample surface through a 400/430 μm multimode optical fibre and lens. The excitation beam was made to be incident at an angle of about 20° to the sample normal in order to prevent the specular reflection coupling back into the collection optics. The fluorescence emanating from the excitation spot was filtered by a 580 nm cut-on interference filter and imaged by a lens onto the end face of a 400/430 μm optical fibre 20 m in length, connected to a CCD array spectrometer (Ocean Optics S2000). The fluorescence excitation and emission spectra of R101 have been discussed in [1].

The fluorescence signal S_F was integrated by summing the spectrum channels between 550 and 750 nm and was recorded as the total number of counts captured during the spectrometer
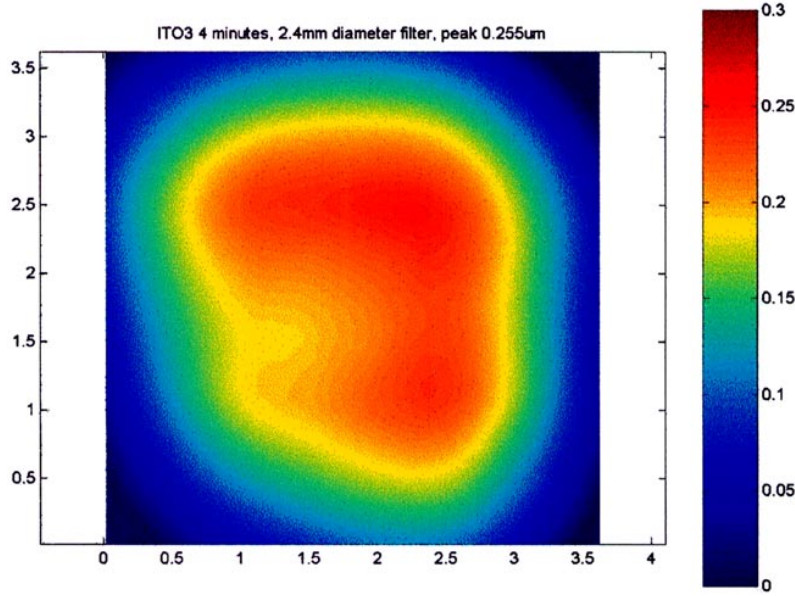
Figure 3. A thickness map of a calibration sample, of maximum thickness 255 nm, measured by using an optical profilometer. The data have been area-averaged by a 2.4 mm diameter uniform circular filter to smooth high frequency thickness fluctuations. The *x* and *y* axes are in millimetres and the thicknesses (right-hand scale) are in micrometres.

integration time by the CCD array. Reduction of the signal due to photobleaching was observed only over several hours, therefore no correction for the timescale of the calibration measurements was necessary.

The main factors determining the fluorescence response have been given in equation (3). They are the thickness *z* of the doped layer, the concentration *D* of R101 dye in the layer, the optical excitation power $P(=AI_0)$ and the spectrometer integration time τ. Calibration was carried out by placing the excitation spot at the centre of the nominally 4 mm × 4 mm sized samples and recording the integrated fluorescence signal S_F for a known set of conditions for *D*, *P* and τ. S_F is plotted in figure 4 against the peak area-averaged thicknesses measured by the laser triangulation technique discussed above. Figure 4 shows the resulting calibration for six samples doped with R101 dye at the concentration $D_{cal} = 0.15\%$, with an excitation power of $P_{cal} = 3$ mW and a spectrometer integration time $\tau_{cal} = 100$ ms. The slope of the linear fit was 0.11 ± 0.05 kcounts nm^{-1}; the fit was not constrained to pass through the origin since no background had been subtracted. The correlation coefficient (R^2) of the line fit was 0.51. Most of the scatter in the data is attributed to the spatial variation in thickness of the calibration films, the structure which can be seen in figure 3. The number of data points in figure 4 was limited to the set of calibration samples that could be produced in the time available.

In general, for measurements on foil coatings without an aluminium layer, *D*, *P* and τ may be made to differ from the calibration conditions in order to optimize the signal-to-noise ratio and the use of the dynamic range of the spectrometer. The above calibration factor is applicable only under the specific conditions of $D_{cal} = 0.15\%$, $P_{cal} = 3$ mW and $\tau_{cal} = 100$ ms for Al-coated ITO samples. In order to correct for a measurement made under conditions *D*, *P*, τ, we apply a linear scaling to obtain a fluorescence signal equivalent to the
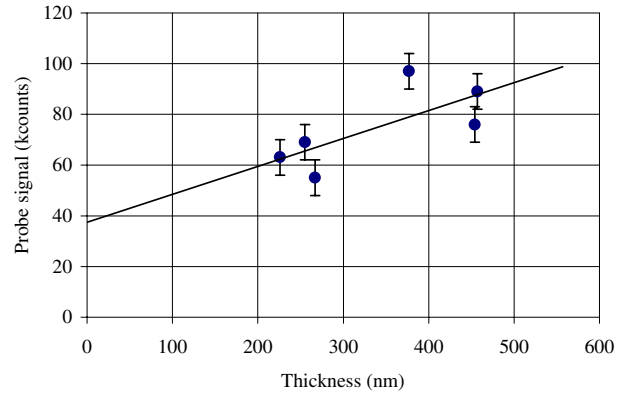

Figure 4. The linear fit to the plot of the fluorescence probe output signal against the maximum thickness of the calibration sample (six points, $R^2 = 0.51$).

calibration conditions:

$$S_{F,corr} = 2k_{substr}\frac{\tau_{cal}}{\tau}\frac{P_{cal}}{P}\frac{D_{cal}}{D}S_F \qquad (4)$$

where k_{substr} is the factor accounting for the quenching of the fluorescence by the aluminium layer on the substrate, as discussed above, with a value of $k_{substr} = 0.10 \pm 0.02$. The factor of two accounts for the double passage of light in the calibration coating after reflection by the aluminium layer, in comparison with a single passage for transparent polymer foil substrates. The thickness *z* of a coating layer on foil is therefore given by

$$z = S_{F,corr}/m \qquad (5)$$

where *m* is the slope of the linear calibration fit.

5. Discussion

We have shown that wax films doped with R101 can be deposited onto a rigid flat substrate to permit an absolute thickness calibration of the fluorescence signal. The electrospray process has been suitable for building up wax films 220–450 nm thick, which we measured by using a laser triangulation profiler. The extrapolation to measurement of thinner films was tested by applying the calibration procedure of equations (4) and (5) to on-line fluorescence signals measured in-process for doped release coatings in industrial trials with $D = 0.051\%$, $P = 3$ mW and $\tau = 500$ ms. Using the slope from figure 4, a release coat thickness of 13 ± 6 nm was obtained, in agreement with bulk area-averaged estimates from measurements of the take-up of solution on the coating plant. Hence the calibration derived from the electrosprayed films is consistent with the existing industrial estimate.

The error in the thickness measurement consists of random and systematic components in the signal S_F and error in the calibration itself. In trials on the industrial coating machine, random measurement error is typically 2%, of which about 0.5% is noise and counting statistics in the CCD array; the systematic error from setting up the probe alignment relative to the target material is typically 5%. The largest contribution to the calibration error is the scatter in the data points in figure 4, resulting in a 45% error in the slope m. For the particular application to monitoring release coat thickness, this is a tolerable error, since it is the relative variation during coating, rather than absolute thickness, that is significant.

Previously reported calibration methods for fluorescence-based thickness measurements have used stylus profilers and optical techniques for thickness measurement [2–5]. In our case, the requirement to use doped wax films has limited the range of applicable techniques for manufacture and measurement of calibration samples. We have shown that laser triangulation profiling of electrosprayed films is suitable for independent thickness measurement in the sub-micrometre range. The calibration (figure 4) yielded thickness measurements in industrial trials that were compatible with the large-area estimates derived from the consumption of coating in the process.

6. Conclusion

Detection of fluorescence emission from a low concentration of fluorophore uniformly mixed into a coating material is a sensitive method of measuring the thickness of a dielectric (wax) coating in the nanometre range that is robust enough for use in an industrial process. A relative calibration verified the linearity of the emission as a function of the amount of fluorophore excited in fluorescent-doped wax film samples. We have addressed the problem of absolute thickness calibration of the fluorescence measurement of very thin solid films by using an electrospray method to make calibration samples suitable for independent thickness measurement. Fluorescent-doped wax films a few hundred nanometres thick have been deposited by electrospraying onto an optically flat glass substrate coated with an aluminium conducting layer. Two-dimensional maps of the wax coating thicknesses were determined using an optical laser profilometer. Fluorescence emitted from the samples was measured using a fibre-coupled probe with laser excitation and spectral detection. The fluorescence emission was shown to be reduced by a factor of ten by the presence of the aluminium layer. The calibration yielded thicknesses of industrial foil release coatings determined by on-line fluorescence measurement that were in agreement with thicknesses estimated from bulk measurement of the take-up of solution in the coating process.

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