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Anti-Counterfeit Solution from Organic Semiconductor

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Abstract

Together with prevalence and price reduction of advanced printing technologies, as well as rapid prototyping appliances, genuine marking becomes a great challenge for manufacturers who want to protect their products from counterfeiting. This challenge can be approached by application of unique marking techniques, based on stochastic generation of markers. This paper describes a technique to fabricate such unique markers, as well as practical approach for in-field marker identification. Evaporation of parahexaphenylene (p6P) molecules in high vacuum system leads to formation of stochastic arrangement of nanofibers in, which can be revealed by ultraviolet illumination, and captured by a portable digital camera through 5x objective. Extraction method for characteristic feature identification is proposed, and genuineness validation protocol is suggested.

Keywords: p6p; nanofibre; molecular beam epitaxy; nano tag;nano marker; pattern recognition; genuine marker; image processing

1. Introduction

Studies of epitaxially surface grown crystalline parahexaphenylene (p6P) nanofibres are one of the major topics of the NanoSyd group at University of Southern Denmark since 2001[1]. Due to their interesting morphology, optical and electrical properties, p6P nanofibres have been used in a variety of applications such as organic field effect transistors[2], organic electroluminescent diodes[3], waveguides[4] or lasers[5]. Their characteristic dimensions are nanoscaled in width and height (100-300nm x 50 100nm)[6], while their length is in range of hundreds of micrometers. The most important properties of p6P nanofibres used in nano tag application are the geometry of their growth and fotoinduced fluorescence.

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With usage of muscovite mica as a substrate, the p6P fibres grow predominantly with 15˚ tilt to the crystal lattice, while narrow distribution of off axis angles is observed.[6] Dimensions and density of fibres depend strongly on deposition conditions[7] such as temperature (around 453±2K), pressure (10-8 mbar) and deposition rate (0.045±0.015Ås-1)[8].

Photoinduced luminescence emission spectra of p6P nanofibres exhibit sharp emission intensity peaks around 425nm, 450nm and 480nm wavelengths, while emitted light is strongly polarised in plane parallel to the long axis of the fibre[9]. Abovementioned characteristics make p6P nanofibres relatively easy to observe.

Although nanofibres are hardly visible in ambient light, UV illumination makes them glow with intense blue colour, the spectrum of which is easy to validate. Moreover, strong polarisation of emitted light gives further possibility for authentication. On samples with lower densities of the fibres, single ones are easily discernible under as low as 5x magnification. It allows usage of a simple optical setup to acquire an image of nanofibres, which form a unique pattern for each sample.

With further image processing, similar to fingerprint recognition, distinctive parameters of the sample are extracted. Such data sets can be compared with a reference entry in a database, which provides a reliable method of authenticity validation.

2. A nanofibre tag

A nanofibre tag produced by NanoSyd, is in a form of 5mm diameter disc. The substrate is muscovite mica, on which there are deposited p6P nanofibres with usage of molecular beam epitaxy. Such a disc can be glued to a surface and protected by lamination. The thickness of such a tag is below 0.3mm.

2.1. Production process

Muscovite mica discs are cleaved with usage of adhesive tape, which leaves the surface atomically flat. Substrates are then placed on a holder, which is composed of mounting plate, heating wire, thermocouple and mounting grill. The holder is being mounted in high vacuum chamber shown in Figure 1.

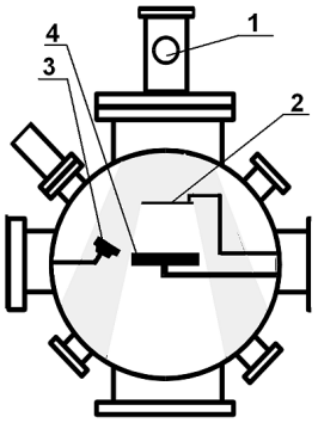

Fig. 1. High vacuum p6P organic molecular beam deposition system: 1) Knudsen cell, 2) shutter, 3) microbalance, 4) sample holder.

The system consists of a Knudsen cell filled with p6P molecules 1 with shutter 2 - for molecular beam formation and control; microbalance crystal - the deposition rate sensor 3, and the sample holder 4. After sealing of the system and pumping it down to desired pressure, both Knudsen cell and sample holder are heated up to their desired temperatures, while molecular beam shutter is kept closed. A Knudsen cell is a device to form a molecular beam. It consists of a closed chamber containing material to be deposited, heater, and an orifice, through which molecular beam leaves the cell when cell is heated up. Due to closed shutter, the beam is unable to reach the substrates, but molecules of p6P are deposited on the microbalance. A Microbalance is an instrument which can precisely measure the mass on its surface, as the resonance frequency of its main part – quartz crystal, strongly depends on surface

load. Microbalances can measure mass increments in range of nanograms.

At this stage of the process, temperature of the Knudsen cell is fine tuned to obtain desired deposition rate shown by microbalance. When deposition rate is stable, the shutter is opened to expose substrates to the molecular beam. Temperatures of sample holder and Knudsen cell are precisely controlled to maintain deposition parameters during all the duration of the process, which ends when a proper mass of p6P have been deposited. The deposition process is done through a grill made of round rods. These rods shadow certain areas of substrates from direct deposition, but their roundness allows mobile particles to form fibres underneath the rods.

When desired amount of material is deposited, the shutter is being closed and both sample holder and Knudsen cell are slowly cooled down to room temperature. Then the pressure is slowly raised to ambient level, when the chamber is being opened and samples are removed.

3. Pattern recognition

3.1. Image acquisition

The image obtained with usage of CCD camera and 5x objective is presented in Figure 2(a). One can observe there three domains: 1.Intense blue regions, which were directly exposed to the molecular beam and are filled with a layer of parallel nanofibres; 2.dark regions which were under the mask, where no nanofibres were formed; 3.transient region near the borders, which were shadowed by mask from direct beam, but mobile molecules continue to grow fibres underneath. The third region is the one of our interest.

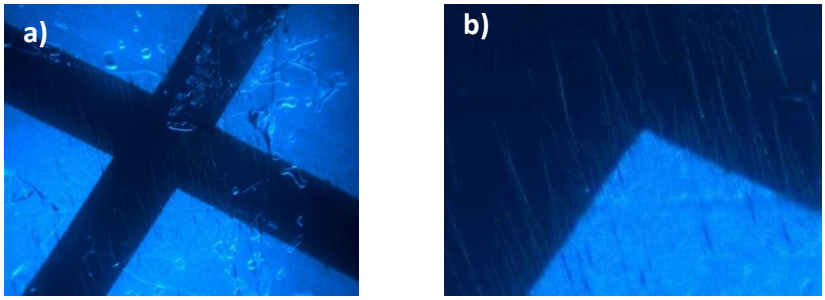

Fig. 2. (a) Image of a nanofibre tag captured by CCD camera with 5x objective; (b) region of interest (ROI) selected from image presented in Figure 2(a).

3.2. Image processing

Image processing starts from selection of the region of interest (ROI), which is presented in Figure 2(b). Image processing chain starts with colour filtering, and converting into greyscale. With usage of morphological operations and image arithmetic, domain 1 is removed from the ROI (Figure 3(a)), while remaining features are enhanced and then threshold to form a binary image. Resulting image is subject to morphological thinning which finalizes processing chain (Figure 3(b)).

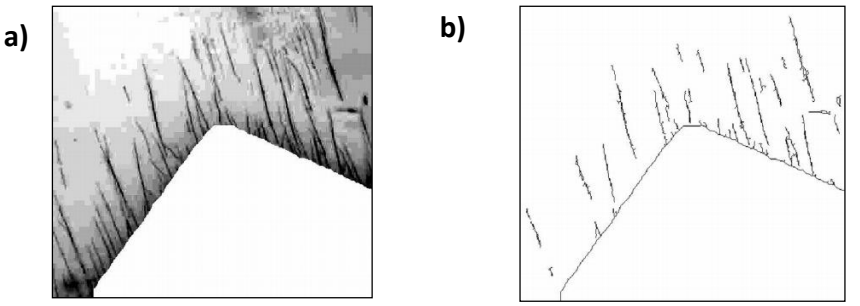

Fig. 3. (a) ROI with domain 1 removed, (b) Image processing chain output.

3.3. Data extraction

Processed image consists of two types of lines: baselines being the borders of masked region, and lines representing fibres which have grown under the mask. As was mentioned earlier, the angle at which those fibres grow, and especially the coordinates of their terminators are stochastic parameters. Therefore this information derived from the image will be unique for each sample.

The tool which is used for deriving those data is the Radon transform. It is the integral transform, which integrates the image over straight lines with baseline inclination and bin position as parameters. Example of transform of square for one particular angle is presented in Figure4(a). Total transform results in an m by n sized matrix, where m is number of bins on x' axis from Figure 4(a), and n is number of angles at which image is being analysed. Sinogram (output of Radon transform) of our output image is shown in Figure 4(b). Here each maximum represents detected line. One can easily identify two major maxima at (63˚, -40) and (145˚, -35), which correspond to border lines; and number of maxima at abscissas around 17˚, which indicates nanofibres.

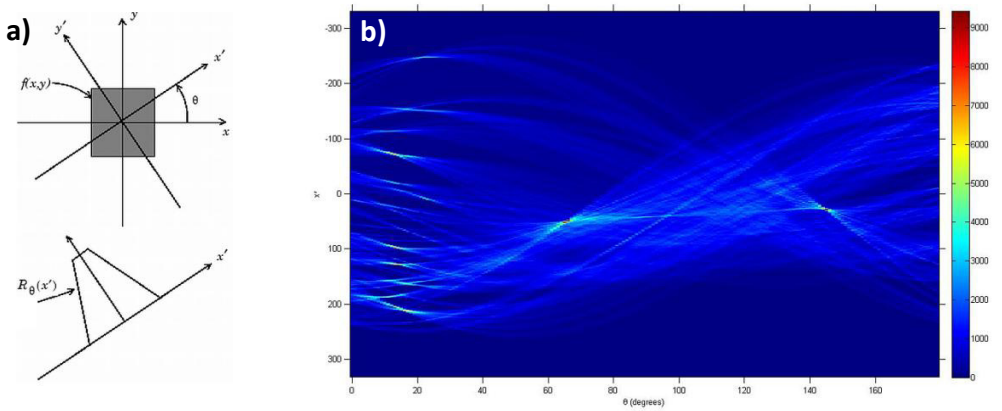

Fig. 4. (a) Diagram presenting Radon Transform principle; (b) Sinogram of the image presented in figure 3(b).

Relative positions of fibre maxima referred to those of border lines are directly interpreted as angles of incidence of fibre and border, as well as their distance from the centre of the ROI. This set of relative coordinates is truly unique for each sample. To ensure robust authenticity proof, parameters of a number of the most distinct fibres are selected and used as digital fingerprint.

4. Conclusion

A nanofibre tag developed by NanoSyd is a versatile and robust answer, for the increasing market demand for

secure authenticity marking. Irreproducible patterns manufactured in stochastic bottom-up growth process and usage of very specific organic material makes it extremely difficult and expensive to counterfeit, while mass production cost is foreseen to be lower than 0.12€ per tag. Low demands on detection hardware enable the possibility of utilising existing devices like smartphones or PDA's, with an add-on optical adapter. Further development aims at a feasibility study of up-scaling the production process to a yield of 1 000 000 tags annually, which is the requirement from an industrial investor interested in venture enterprise.

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