50 & 100 YEARS AGO

50 YEARS AGO

The Spirit of Liberty: Papers and Addresses of Learned Hand — The papers and addresses collected in this book range for the most part over fields with which the man of science is concerned rather as citizen than as scientist...Supremely the book testifies to the truth of Judge Hand's contention that there is no substitute for an open mind enriched by reading and the arts, and that the scientific worker who would influence the thought and action of his time must have some acquaintance, the wider the better, with what others have thought and felt in circumstances as near as possible to those of the groups in question...The plea for the open mind and free discussion in which these words occur is much more than championship of dissent and a direct rebuke to the excesses of McCarthyism and secrecy and security procedures: it is an outstanding statement of the case for general education as the basis of a free society.

From *Nature* 17 September 1955.

100 YEARS AGO

At the present time by far the most serious problem which the automobilist has to face is the abatement of the "dust nuisance". A great deal of bad feeling has arisen against the motorist on account of the dust which he too frequently produces, and there is no doubt that there are very good grounds for the irritation which has arisen, particularly in agricultural districts...Although a permanently good road may be made by the use of materials such as Tarmac, and dusty roads may be cured temporarily by various means, yet such measures can be taken only over a small proportion of our roads owing to the cost. In towns and large villages the roads might be suitably treated, but the average motorist seeks the country, and the greater part of the routes which he wishes to traverse will not pay for any special treatment.

From *Nature* 14 September 1905.

in a vacuum, or the wet-chemical deposition of polymers onto a substrate. Which of these approaches will ultimately survive in a production environment is still a matter of debate. Although the small-molecule approach improved device performance, especially device lifetime, wet-chemical deposition is the more attractive technique for mass production. This is because it allows layers of polymers to be laid down cheaply in a roll-to-roll process using common techniques such as those used for screen and inkjet printing. It is therefore the method of choice for Gong *et al.*[2] and many others.

Multi-layer OLEDs are generally more efficient than single-layer types. In the most efficient OLEDs, the emission layer is sandwiched between a hole-transport layer and an electron-transport layer (Fig. 1). Fabricating such multi-layer structures from solution is challenging (vacuum deposition of small molecules is relatively straightforward). It is crucial to ensure that layers already deposited from solution are totally resistant to the solvents used to deposit subsequent layers, to avoid intermixing.

There are three main ways to do this. The first is to use 'orthogonal' solvents for the individual layers — that is, the solvent used in one deposition does not dissolve any previous layer. For example, the conductive polymer poly(3,4-ethylenedioxy)thiophene (PEDOT), commonly used for OLED anodes, is deposited from an aqueous suspension. After drying, further organic layers can be deposited from typical organic solvents such as toluene without redissolving the PEDOT. A second method is to change the polarity or solubility of the deposited material. An example here is the first luminescent polymer ever discovered, poly(*p*-phenylenevinylene), or PPV (ref. 4), where a polar sulphonium precursor molecule is transformed by heating into a nonpolar polymer that is insoluble in all organic solvents.

A third, highly attractive approach is to introduce several reactive molecular groups into a semiconductor material. These can be polymerized after deposition to yield totally insoluble crosslinked layers, a process that can, in principle, be repeated indefinitely. In recent years, many materials that can be processed from solution and possess the ability to form multi-layers have been proposed, the most promising being oxetanes[5], styrenes[6], dienes[7] and trifluorovinyl ethers[8]. The efficiency of OLEDs at incorporating such materials (most of which are hole-transporters) is in many cases greater than that for reference devices using just PEDOT as anode, or the transparent metal indium tin oxide (ITO).

Gong *et al.*[2] propose an extension of the first, orthogonal-solvent approach. They developed derivatives of two commonly used organic semiconducting materials — the hole-conducting poly(*N*-vinylcarbazole), or PVK, well known from the early days of xerography, and the electron-conducting oxadiazole derivative PBD. The authors achieved this by incorporating into them ionic sulphonate groups, which make the derivatized material soluble in highly polar solvents such as water and ethanol but insoluble in organic solvents. This trick allowed them to create the layers using aqueous or ethanol solution, as the components of the emissive layer of the OLED were totally insoluble in either solvent. (The emissive layer contained a fluorescent polymer emitting green and blue light, doped with a phosphorescent molecule that sends out red light, yielding an overall white emission.)

By alternating deposition from hydrophilic and hydrophobic solvents, Gong and colleagues built a three-layer device (Fig. 1). Because the emissive layer acts as a barrier against the redissolution of the first deposited layer (the hole-transport layer) during the deposition of the third layer (the electron-transport layer), it was of crucial importance that all layers were free of pinholes. The resulting OLEDs produced a luminous intensity of around 10 candelas per ampere of supplied current — around 2.5 lumens per watt. The efficiency of the device is thus among the highest to date for solution-processed white-light-emitting devices[1], and one-and-a-half to three times better than reference devices in which either of the two transport layers was missing.

It might be thought that the introduction of sulphonate groups and the consequent presence of mobile metal counter-ions might impair the device's performance. Certainly, devices using transport layers show slightly increased onset voltages — the minimum supply voltage at which emission will occur. According to Gong and colleagues, this is due to the greater thickness of the device compared with other OLEDs and could thus presumably be improved by adjusting the layer thicknesses, or by using different hole- and electron-transport materials containing sulphonate ions or other ionic groups.

The big question, however, is whether devices based on such sulphonate materials can reach the operating lifetimes necessary for practical applications (typically more than 10,000 hours). The presence of mobile metal ions could cause similar problems here to those seen with electrochemical emissive devices. Although such questions remain unresolved, Gong and colleagues' contribution[2] is a step towards a more flexible, lower-cost source of white light. ■

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