Advances in PEDOT:PSS Conductive Polymer Dispersions

Ronald P. Lubianez*, Stephan Kirchmeyer§, Detlef Gaiser§
*H.C. Starck, Inc., 45 Industrial Place; Newton, MA 02461 USA, Phone +1 (617) 630-4893
§H. C. Starck GmbH, Chempark, Building B 202, 51368 Leverkusen, Germany

Abstract

Roll-to-roll manufacturing of flexible electronics requires easily applied transparent conductors. H.C. Starck offers environmentally friendly alternatives to the vacuum sputtered conductive oxides (TCO) that have been extensively used in these applications. Clevios™ dispersions based on poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) featuring high conductivity, transparency and low cost will be discussed. Clevios™ coatings can be applied by many coating and printing techniques. A new 600 S/cm-conductivity grade will be discussed for TCO replacement in flexible displays, touchscreens, and organic photovoltaics.

Introduction

During the last 10 years the Inherently Conducting Polymers (ICP) have evolved from laboratory to mature commercial products. Polythiophenes are one prominent class of ICP presently in the market. Poly-(3,4-ethylenedioxythiophene) (PEDOT) which has been marketed by H.C. Starck GmbH under the trade name **CLEVIOS™** (formerly BAYTRON®) currently plays a significant role in antistatic, electric and electronic applications. Widespread applications have been developed utilizing the conducting properties of the poly-(3,4-ethylene-dioxythiophene) complex with polystyrene sulfonic acid (PEDOT:PSS) as well as the *in situ* polymerized layers of the 3,4-ethylenedioxythiophene monomer (*in situ*-PEDOT). PEDOT is the predominant counter electrode in both aluminum and tantalum polymer capacitors. Such polymer capacitors serve as a first demonstration of an electronic device using a polymeric functional material. Various and expanding uses for PEDOT:PSS include antistatic layers e.g. for photographic films or as protecting films during assembly of flat screen displays.
Various and expanding uses for PEDOT:PSS include antistatic layers e.g. for photographic films or as protecting films during assembly of flat screen displays. However, highly conductive transparent films, such as are required for applications in which ITO is routinely employed, have remained until recently largely unattainable using PEDOT:PSS. Over the last few years, though, research aimed at a deeper understanding of the polymer's chemical properties, mechanism of conductivity, and processing parameters has enabled the development of dispersions that can be used as transparent conductors in a variety of devices, such as inorganic electroluminescent displays, liquid crystal displays, organic light-emitting diodes, all-organic field effect transistors and organic photovoltaics. In this presentation we will give an overview of PEDOT:PSS properties and how they are utilized and optimized to produce highly conductive films, and then several examples of applications using PEDOT:PSS films as device electrodes are highlighted.

THE CHEMISTRY OF PEDOT:PSS

The PEDOT:PSS-Complex Formed by Template Polymerization with PSSA

Commercially available dispersions of PEDOT:PSS are made by aqueous oxidative polymerization of the monomer 3,4-ethylenedioxythiophene (EDOT) in the presence of the template polymer polystyrene sulfonic acid. (PSS or PSSA) (Figure 1). The PSS in the complex functions as a counter ion for the cationic, conductive PEDOT and also allows the formation of a stable, easy-to-process dispersion of PEDOT:PSS polymer gel particles. These gel particles consist roughly of 90 to 95 % water in the dispersion, have excellent film forming properties, and are easily processable into thin coatings on a variety of substrates.

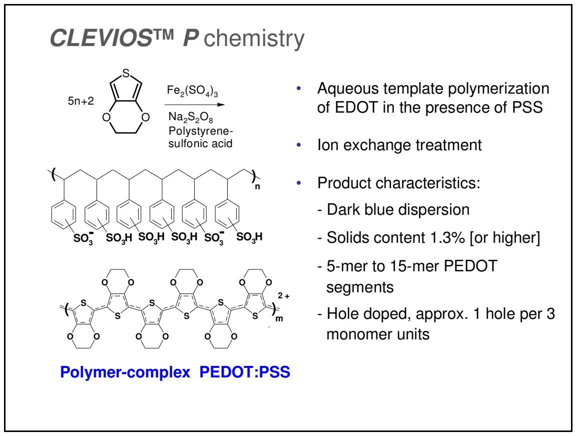


Figure 1: Template polymerization of EDOT in the presence of PSS to form PEDOT:PSS dispersions of conductive polymer

Structure of the PEDOT:PSS Complex

A structural model for the structure of PEDOT:PSS is shown in Figure 2. In this model, oligomeric PEDOT segments are tightly, electrostatically attached to PSS chains of much higher molecular weight. The high conductivity of PEDOT:PSS dispersions can then be attributed to stacked arrangements of the PEDOT chains within a larger, tangled structure of loosely crosslinked, highly water-swollen PSS gel particles. In dried PEDOT:PSS films, boundaries—*i.e.* energy barriers—between the dried gel particles in a film contribute significantly to the overall resistivity of the film. Maximum conductivity is achieved by maximizing the contact between dried gel particles in PEDOT:PSS films. Therefore, the highest conductivities are achieved either (a) when the particles are largest, *i.e.* when the total number of particle boundaries in a given volume or area is minimized, or (b) when there is significant intermingling of individual gel particles, which reduces the effective number or “size” of the particle boundaries.

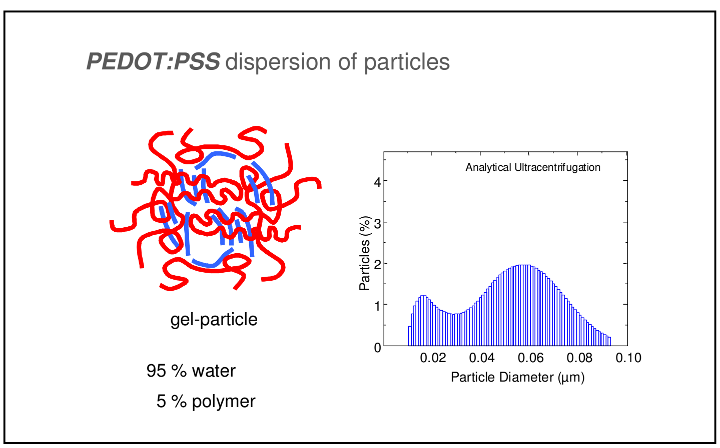


Figure 2: Schematic depiction of PEDOT:PSS structure

Conductivity Enhancement Agents

Through the use conductivity enhancing additives (Figure 3) it is possible to increase the conductivity of PEDOT:PSS from initially less than 10 S/cm to more than 500 S/cm. This development has opened a window for the use of PEDOT:PSS in applications which seemed to be reserved for transparent metal oxides like indium tin oxide. A very important class of additives for making highly conductive PEDOT:PSS films is ***high boiling solvents***. Particularly useful are polyhydroxy compounds like ethylene glycol, and sulfoxides like dimethylsulfoxide. Amides such as N-methylpyrrolidone can also be utilized. These solvents, often called "secondary dopants"[1] or "conductivity enhancement agents," are used in small amounts to increase the conductivity of the final, dried film. The effects of these additives are independent of whether they remain in the film after drying or not. The most common interpretation is that the polar solvents at least partly dissolve the PEDOT-stacks in the PEDOT:PSS complex, thereby creating an opportunity for a favorable morphological rearrangement and clustering of gel particles. The rearrangement leads to a decreased resistance between dried gel particles, thus increasing the overall conductivity of the film.

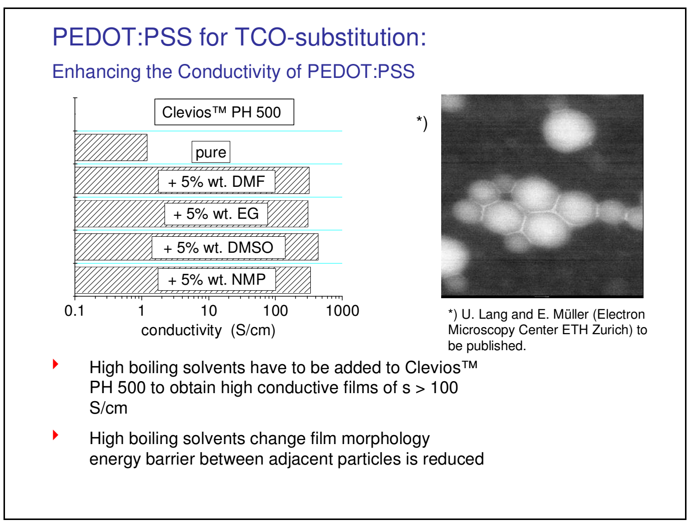


Figure 3: Conductivity Enhancement of PEDOT:PSS

Other Coating Formulation Ingredients

Other common formulation components and their effects on PEDOT:PSS films are as follows.

- Organic co-solvents are added to adjust the surface tension of PEDOT:PSS dispersions, thereby improving the wetting and general coatability of the polymer on hydrophobic substrates such as polyesters, polycarbonates, polyethylenes, and other polymer film bases. The use of volatile co-solvents, such as ethanol and isopropanol, can also be used to decrease drying times.
- Non-volatile wetting agents and surfactants can also be added to adjust dispersion surface tension and coatability. Because the solids contents of the aqueous PEDOT:PSS dispersions are usually rather low (between 1.5 and 4%), and because non-volatile additives will likely accumulate in the dried films, these additives are effective at extremely low loading levels. For example, a surfactant that has been added to the PEDOT:PSS coating formulation at a 1% loading level will make up as much as 30% of the final, dried film.

- Polymeric binders – often waterborne polyesters and polyurethanes—are added to improve the adhesive and mechanical properties of PEDOT-based films. Especially in cases where plastic substrates are coated by PEDOT:PSS and subsequently mechanically treated after coating, such as by thermoforming, addition of a binder to the PEDOT:PSS can help to maintain the overall conductivity by maintaining particle-particle connectivity. Choice of binder varies with the targeted properties of the final film. Polymeric binders can also be used as a nonconductive matrix material for increasing the overall surface resistivity of a film. For example, if an antistatic coating surface resistivity of 10^8 Ohms/square or higher is targeted, a high percentage of binder is employed. For lower surface resistivities, lower binder percentages are used.
- Silanes, tetraalkylorthosilicates, and similar compounds can be added to increase the adhesion to the underlying substrate or to increase the hardness and wear resistance of the conducting film.

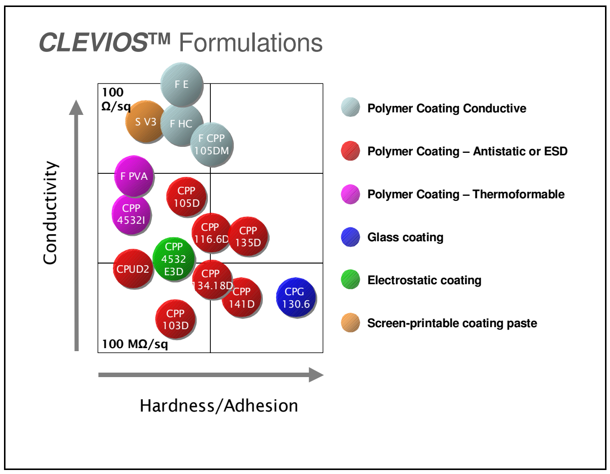


Figure 4: Conductivity Range of CLEVIOS™ Formulations

APPLICATIONS EMPLOYING HIGHLY CONDUCTIVE PEDOT:PSS DISPERSIONS
Electrically Conducting Coatings
Conductive materials are used as electrodes for the operation of electronic devices, and in most cases the current density required for device operation is several orders of magnitude higher than that required for protection against antistatic discharges. In many device configurations, especially in various types of displays, it is often also required that the conducting electrode layers be transparent. Indium-tin-oxide (ITO) is the industry's most commonly used transparent conductor material, especially in display markets, but while these markets continue to grow, indium prices are also rising as supplies of indium are becoming more and more limited. Therefore, alternatives to ITO are sought. Today PEDOT:PSS types are available with sufficient conductivity to serve as electrodes in many electronic devices. Over the last decade, great progress has been made in efforts to synthesize higher conductivity versions of PEDOT:PSS as shown in the trend line of **Figure 5**. PEDOT:PSS dispersions with inherent conductivities as high as 600 S/cm have been produced on a Pilot Plant scale.

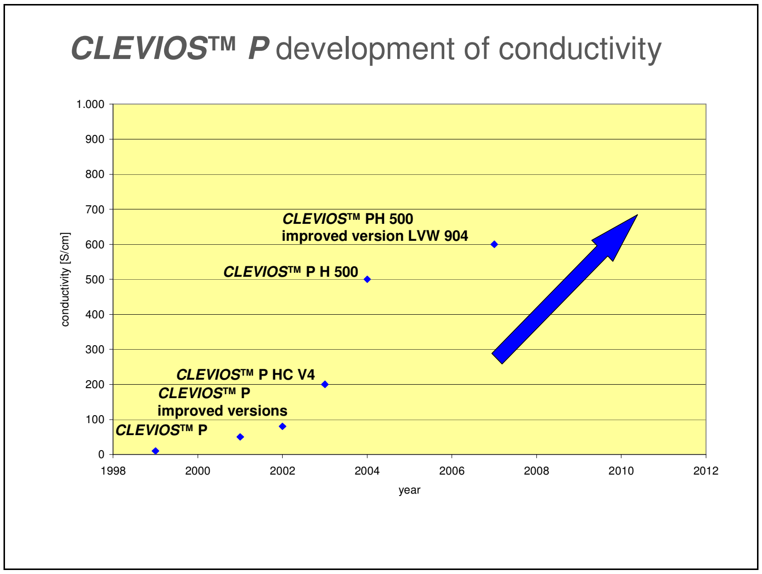


Figure 5: Development of High Conductivity Grades of CLEVIOS™ P

Besides lower processing costs, an additional technical advantage to the use of PEDOT:PSS as a transparent conductor is the flexibility of the contact layer. ITO is a brittle, inorganic material not ideally suited to destruction-free thermal deformation. In contrast, devices fabricated with transparent, conductive PEDOT:PSS electrodes can be made highly-flexible and, in some cases, can even be designed for three-dimensional thermoforming. A comparison of the flexibility of PEDOT:PSS films and ITO films is shown in **Figure 6.**

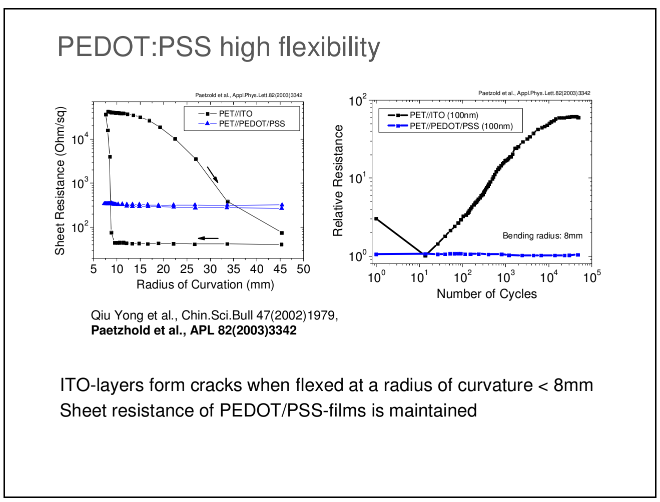


Figure 6: Comparison of Flexibility Between PEDOT:PSS and ITO Coated Films

Inorganic electroluminescent (EL-) devices comprise a composite active layer of a zinc sulphide emitter and a dielectric such as barium titanate sandwiched between two conducting layers, one of which must be transparent. When an AC voltage of approximately 100 V/400 Hz is applied, the zinc sulphide emits light, the hue of which can be tuned by the addition of appropriate doping agents. **Figure 7** shows a schematic of the layered structure of typical EL device in which the transparent electrode is made with PEDOT:PSS.

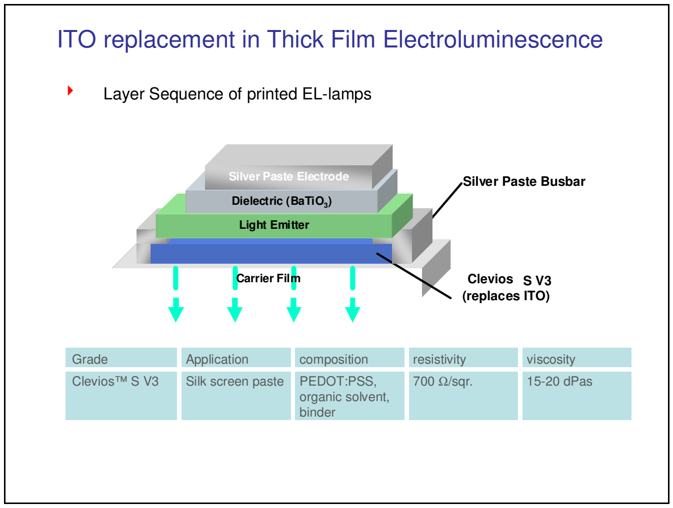
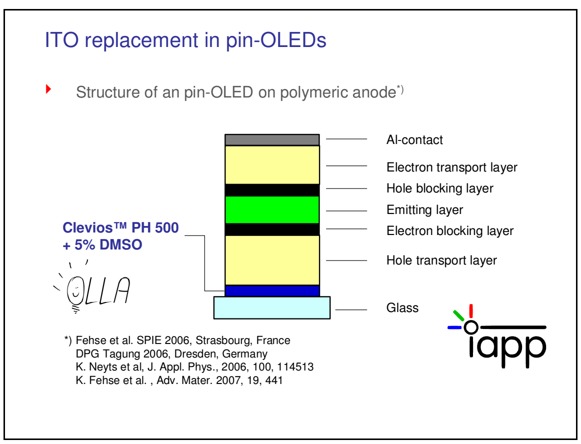
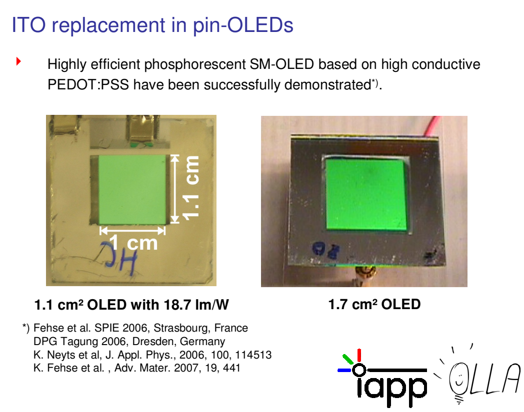


Figure 7: PEDOT:PSS Electrode in Thick Film EL Device

Electrodes in current driven organic devices such as organic light emitting diodes (OLEDs) or organic solar cells (OSCs) have been made from PEDOT:PSS as a replacement of ITO. Although the conductivity and the transparency of PEDOT:PSS layers are significantly lower compared to high-quality ITO the principle proof to employ conductive polymers in these applications has been demonstrated. An example has been shown within the EU funded OLLA-project. During this project we have jointly developed an ITO-free pin-OLED lamp (**Figures 8 and 9)** made with PEDOT:PSS as transparent electrode.





Figures 8 and 9: Replacement of ITO Anode with PEDOT:PSS in pin-OLEDs

The roll-to-roll printing of organic electronic devices will require patterning as depicted in **Figure 10.** Fully patterned all-organic TFTs have been fabricated with PEDOT:PSS by conventional structuring techniques, inkjet processing and other patterning techniques like line patterning. While usually gate, source and drain contacts were prepared from PEDOT:PSS some groups even propose PEDOT:PSS as channel material.

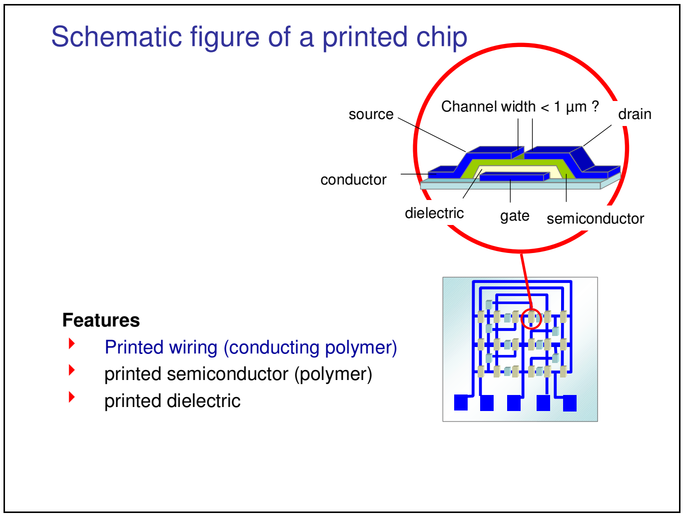


Figure 10: Diagram of Thin Film Transistor

Commercial formulations have been developed that are applicable in screen printing (Figures 11 and 12).

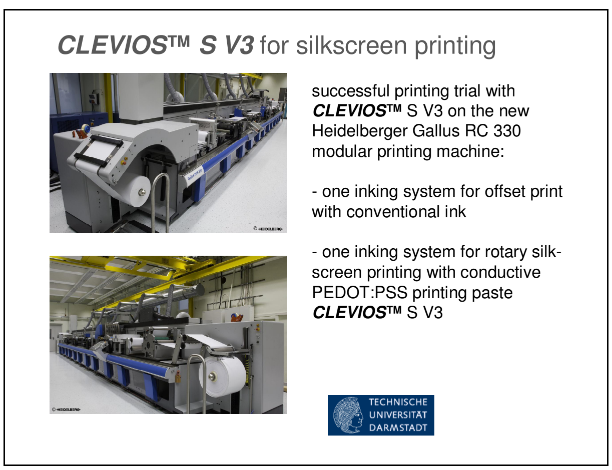


Figure 11: Modular Printer at Technische Universitat Darmstadt

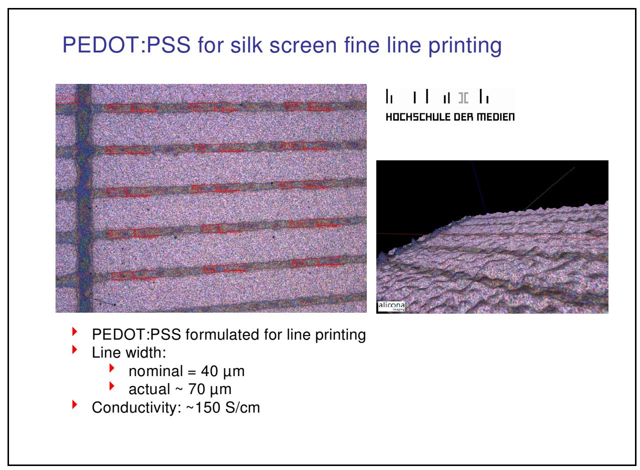


Figure 12: Screen Printed Lines of PEDOT:PSS

Inkjet printing is a technique that has received attention with respect to the high volume roll-to-roll printing of organic electronic components due to the ability to print fine lines and wide areas. It is utilized commercially in the printing of flexible packaging and formulations of PEDOT:PSS have been developed for inkjet printing with a range of conductivities (0.0002 to >200 S/cm). The modifications of the formulations have been made through the adjustment of solids content, viscosity and surface tension.

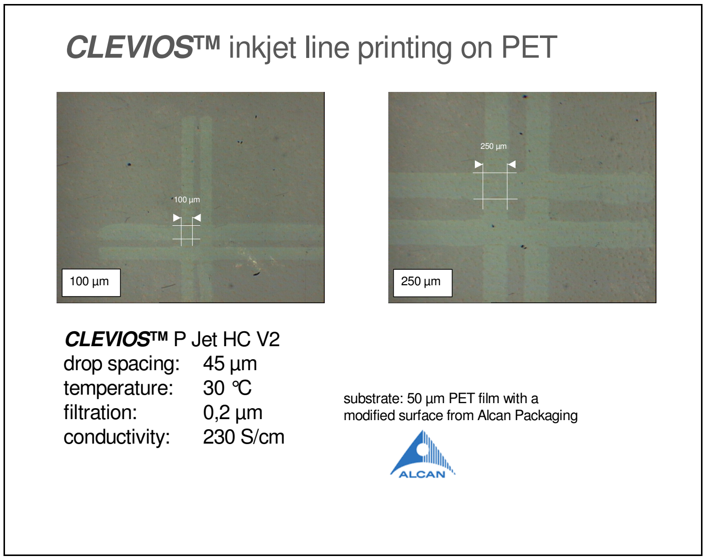


Figure 13: Conductive PEDOT:PSS dispersions for Inkjet Printing

SUMMARY

Printed electronic devices need suitable materials and processes that still face a number of challenges. One class of materials that is needed is transparent polymeric conductors that can be applied via high quality printing processes. Highly conductive PEDOT:PSS polymer dispersions have been incorporated into coating formulations for several different coating and printing techniques. The coated films from these formulations have been utilized as transparent electrodes and transparent circuitry in printed electronic devices.