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Study of the effect of solvents and surfactants on electrical properties of PEDOT:PSS films

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Abstract. It was demonstrated that non-ionic surfactants reduce the solution's surface tension, improving the wettability of hydrophobic substrates. Even 0.05% of Neonol can significantly affect the surface tension of the aqueous PEDOT:PSS solution on fused silica substrates. However, higher percentages of Neonol increase the electrical resistivity of the polymer layer. For film deposition, a minimum neonol volume fraction of 0.005 vol.% was required. In this work examined how adding different volume fractions of dimethyl sulfoxide affected the electrical conductivity of PEDOT:PSS films. Two methods were used to add dimethyl sulfoxide to the films: the pre-adding method and the post-spin-rinsing method. The electrical properties of the films with and without the addition of dimethyl sulfoxide were measured. Films produced using the dimethyl sulfoxide post-spin-rinsing method exhibited the highest conductivity achieved in this paper, reaching 780 S/cm. The results of time degradation studies conducted during the research demonstrate that the electrical conductivity of the samples, on average, decreased by more than half after a two-week period.

Keywords: PEDOT:PSS, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate, conductive polymer, surfactants, neonol, electrical resistance

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Исследование влияния растворителей и поверхностно-активных веществ на электрические свойства пленок PEDOT:PSS

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Аннотация. Было показано, что неионогенные поверхностно-активные вещества снижают поверхностное натяжение раствора, улучшая смачиваемость гидрофобных подложек. Даже 0.05% неонола может значительно повлиять на поверхностное натяжение водного раствора PEDOT:PSS на подложках из кварцевого стекла. Однако более высокие проценты неонола увеличивают удельное электрическое сопротивление полимерного слоя. Определено, что для осаждения пленки требуется минимальная объемная доля неонола 0,005 об.%. Исследовано как добавление различных объемных долей диметилсульфоксида влияет на электропроводность пленок PEDOT:PSS. Для внесения диметилсульфоксида в пленки использовали два метода: метод предварительного добавления в раствор и метод внесения на осажденную пленку. Измерены электрические свойства пленок с добавкой диметилсульфоксида и без нее. Пленки, изготовленные методом внесения в осажденную пленку, показали наивысшую достигнутую в работе проводимость, достигающую 780 См/см. Результаты исследований временной деградации, проведенных в ходе исследований, показывают, что электропроводность образцов в среднем снижается более чем в два раза после двухнедельного периода.

Ключевые слова: PEDOT:PSS, поли(3,4-этилендиокситиофен) полистиролсульфонат, электропроводящие полимеры, поверхностно-активные вещества, неонол, диметилсульфоксид, электрическое сопротивление

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Introduction

Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), is a type of conductive polymer that is utilized in various applications such as electroluminescent devices, organic light-emitting diodes, and various types of photovoltaic cells [1–3]. Compared to other conductive polymers used in hybrid and organic solar cells, PEDOT:PSS has several advantages, including its passivation effect, high conductivity, optical transparency, mechanical stability, and commercial availability [1, 2].

Pure PEDOT without PSS content exhibits electrical conductivity in the range of tens of S/cm. However, when combined with a counterion, the electrical conductivity can reach several hundred S/cm [3]. The mixture requires PSS as a dispersant and counterion for the PEDOT polycation. At the same time conductivity of the PEDOT:PSS layer decreases as the percentage of polystyrene sulfonate in the initial solution increases. The aqueous dispersion contains hydrophobic and conductive PEDOT particles which are encapsulated by hydrophilic and insulating PSS particles, forming core-shell structures [4].

High-boiling dielectric solvents such as dimethyl sulfoxide (DMSO), ethylene glycol, N-methylpyrrolidone, and dimethylformamide, can alter the configuration of PEDOT:PSS, leading to an increase in conductivity [1, 5].

The spin-coating method is the usual approach to apply PEDOT:PSS films, and two prevalent techniques to incorporate solvents into the film are the pre-adding method (PAM) and the post-spin-rinsing method (PSRM). The pre-adding method (PAM) involves adding solvents directly to the PEDOT:PSS solution before the coating process. Conversely, in the post-spin-rinsing method (PSRM), solvents are applied onto the dried film, followed by spin-coating and baking. The post-spin-rinsing method (PSRM) is known to provide higher electrical conductivity values. On the other hand, the advantage of the pre-adding method (PAM) is that it involves fewer application steps, which can be beneficial for industrial production. The highest electrical conductivity values obtained from the DMSO PSRM reach 1335 S/cm, whereas the highest electrical conductivity value for DMSO PAM is 680 S/cm at 5 wt% DMSO [4].

PEDOT:PSS films, like most other conjugated polymers, are subject to photo-oxidative degradation over time due to exposure to UV radiation and atmospheric oxygen. This process results in a decrease in the electrical conductivity of the coating [3].

Another current problem is insufficient wetting of hydrophobic substrates such as silicon when using an aqueous solution of PEDOT:PSS, which leads to uneven deposition of the polymer coating. The addition of low-boiling solvents and non-ionic surfactants reduces the surface tension of the solution and increases the wettability of hydrophobic substrates with the solution [5].

Proper selection of the initial solution composition and coating method can lead to the deposition of uniform films with improved electrical conductivity.

Materials and Methods

Polished fused silica wafers 400 µm thick were used as transparent dielectric substrates. A 1% aqueous solution (Sigma Aldrich, pH < 2.5, PEDOT:PSS Ratio 1:0.5) was used to form thin layers of the electrically conductive PEDOT:PSS polymer. To increase the wettability of the substrates, a non-ionic surfactant was added to the PEDOT:PSS aqueous solution in the form of a mixture of oxyethylated monoalkyl phenol derived from propylene trimers (Neonol AF 9-12 produced by Nizhnekamskneftekhim PJSC) at a volume concentration of 0.05% to 1%.

Thin PEDOT:PSS films were deposited on the surface of fused silica substrates by spin-coating at 1000 rpm for 60 s. Immediately after spin-coating, the films were baked on a hotplate at 130 °C for 10 min. Samples with the addition of DMSO were applied by two different methods: PAM and PSRM. In PAM-modified samples, the volume fractions of DMSO were used: 2.6 vol%, 9.7 vol%, 12.4 vol%. The content of neonol in the initial solution was 0.5 vol%. The low concentration of neonol used in the series was chosen to achieve optimal electrical properties. In PSRM-modified samples, the volume fraction of neonol in the initial solution was 0.05 vol%. After coating and baking, 100µl of DMSO was applied to the initial film and held for 3 min, and then spin-coated at 4000 rpm for 60 s. After DMSO spin-coating films were baked at 130 °C for 10 min.

The layer thicknesses on the fused silica substrates were measured by contact profilometry on a sharp step between the surface of the layer and the substrate using an Ambios XP-1 profilometer. To measure the electrophysical properties using the Van der Pauw four-point probe method silver contacts 1 mm diameter and 500 nm thick were thermally deposited onto the surface of the structures by vacuum evaporation. The contacts were arranged in a square shape with a side length of 1 cm. Based on the measurement results, the values of the sheet resistance and specific electrical resistance of thin PEDOT:PSS layers on the surface of fused silica with different surfactant concentrations were obtained. Optical transmittance spectra were obtained on an Avantes Avaspec ULS2048XL spectrometer.

Results and Discussion

Transparent PEDOT:PSS films were evenly deposited on the surface of fused silica from an aqueous solution with Neonol concentrations from 0.05 to 1%, which made it possible to study their optical and electrophysical properties. An aqueous solution of PEDOT:PSS without surfactants could not be applied to fused silica substrates due to poor wettability, which leads to the formation of separate droplets after the spin coating stage. There is also a gradual increase in the electrical resistivity of the layers with an increase in the percentage of surfactants (Fig. 1, *a*), which negatively affects the conductive properties. The Fig. 2, *b* shows the dependences of the thickness and conductivity for films obtained by the DMSO PAM. The film conductivity increases with an increase in the volume fraction of DMSO in the initial solution. Also, with an increase in the volume fraction of DMSO, the thickness of the coating decreases, which is caused by a decrease in the PEDOT:PSS volume fraction in the applied solution.

The maximum conductivity for PAM-modified PEDOT:PSS is observed at DMSO volume fraction in a solution of 12 vol.% and is 510 S/cm (0.00195 Ohm·cm), which does not reach the theoretically possible value of 680 S/cm [4]. The conductivity of the films obtained by the PSRM method reached 780 S/cm (0.00128 Ohm·cm), which is the maximum value achieved in this work. The coating thickness was 22 nm.

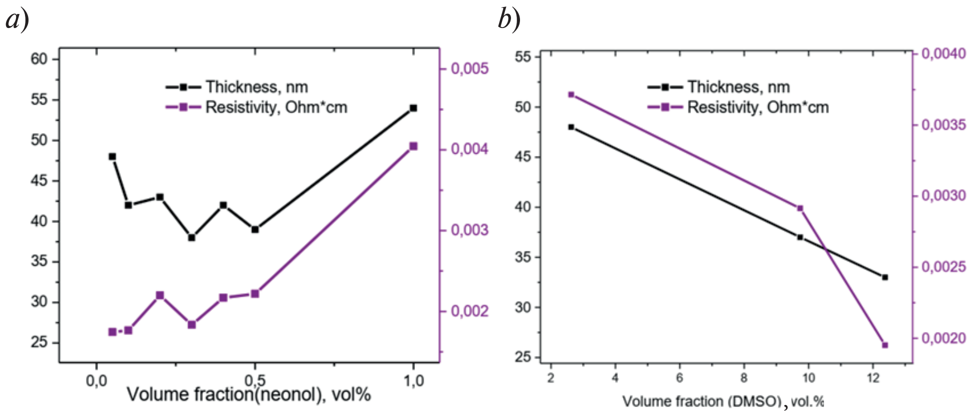

Fig. 1. Dependence of thickness and specific electrical resistance on the volume fraction of neonol in solution (*a*) and PAM-modified samples specific conductivity and thickness dependence on the DMSO volume fraction in initial solution (*b*)

The transmittance of the films in the wavelength range from 500 to 1000 nm is shown in Fig. 2, and the optical transparency mainly depends on the film thickness. As the film thickness increases, the transparency tends to decrease.

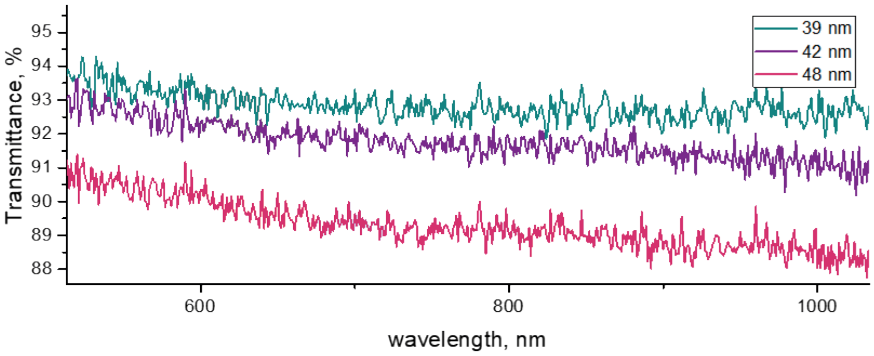

Fig. 2. Transmittance spectra dependance on the film thickness

Studies have shown that the electrical conductivity of unencapsulated PEDOT:PSS films tends to decrease over time when exposed to ambient light and oxygen at room temperature. In Fig. 3, it can be observed that after a period of 14 days, the conductivity of the samples reduced by an average of factor of 2.56.

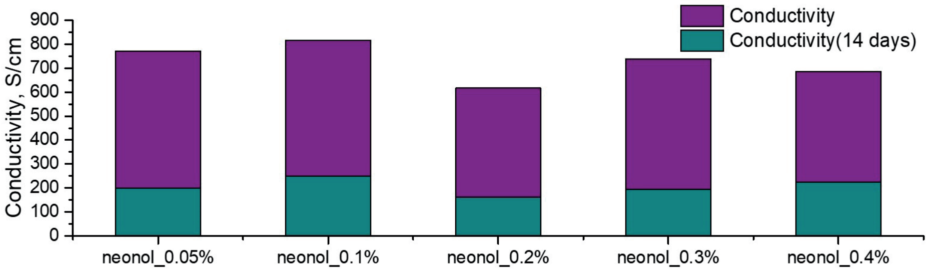

Fig. 3. The Effect of Film Degradation on Conductivity

Conclusion

Thus, the use of Neonol effectively affects the surface tension of an aqueous solution of PEDOT:PSS when applied to fused silica substrates even at a percentage of 0.05 vol.%. A further increase in the percentage of Neonol in solution increases the electrical resistivity, which deteriorates the conductive properties of thin layers of a transparent polymer. As a result, when applying layers of PEDOT:PSS on fused silica substrates, it is recommended to use Neonol to wet the surface of hydrophobic substrates, but at concentrations of 0.05 vol.% or less. The minimum volume fraction of neonol required for film deposition was 0.005 vol.%.

The maximum achieved conductivity of 780 S/cm was found in films obtained by the DMSO PSRM method.

It was found that in two weeks the conductivity of the samples decreases on average by more than two times.

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