

# Electrical properties of $C_{19}H_{20}N_2O_4SW$ based molecular-materials thin films prepared by electrodeposited technique

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**Abstract** Semiconductor molecular-material thin films of Fischer carbene tungsten(0) have been prepared by electrodeposition in the electrochemical module of the atomic force microscope (AFM). This use of the AFM is proposed as a more efficient way to generate molecular materials, as it permits thin-film synthesis to be monitored and manipulated before characterization. The films thus obtained were characterized by infrared (FTIR), AFM and energy dispersive spectroscopy. The molecular material thin films exhibit the same intra-molecular bonds and the chemistry composition as the original compounds. The effect of temperature on conductivity was also measured in these samples: its behavior found as pertaining to a semiconducting material. The activation energies of thin films are determined from Arrhenius plots with these energies being within the range from 0.4 to 1.82 eV. The electrical transport properties for the thin films were determined by their chemical structure.

## 1 Introduction

The need for developing new compounds which may find applications in both optoelectronic and electronic industries,

has generated an ever increasing interest in using materials that were formerly considered as insulators, such as organometallics and organic compounds. The organometallic compounds from transition metals exhibit a synergy between the metallic fragment, and the organic fragment that proves quite interesting for myriad applications in optoelectronics and electronics. Organometallic devices could be competitive for low-cost applications in electronics requiring large area coverage, structural flexibility and low temperature processing [1]. These materials are also known as low dimensionality solids, an example being the TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane), which presents electric conductivity up to  $10^2 \text{ S m}^{-1}$  at room temperature, and which markedly increases up to  $80 \text{ KS m}^{-1}$  with descending temperature [2, 3]. One-dimensional solids are a major field development, because they present new mechanic, chemical, magnetic, optical and electrical properties, among others. In turn, all these features place these materials at a very important place in the development of new technologies, with electronic conduction being most relevant. From organometallic compounds made of transition metals, the carbenes thiomidics stand out, since they behave as building blocks in the presence of low dimension molecular materials [4–6]. On having been treated over suitable bases, the carbenic complexes generate stabilized carbanions which, upon reacting with appropriate electrophiles, give rise to semiconductor organic materials, difficult to obtain by other means. The chemistry of Fischer carbenes or heteroatom-stabilized electrophiles has attracted great interest owing to the low metal oxidation state, to the  $\pi$  acceptor ligands and to the heteroatoms which may donate electronic density to the carbenic carbon atom. Not many papers, however, have been reported regarding the use of Fischer carbenes thin films. All these compounds have become very valuable building blocks in studies of electron transfer processes

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[7, 8]. Recent research work has been oriented to the formation and characterization of conducting thin films [9]. Although chemical vapour deposition has been extensively used to produce molecular films onto conductive substrates typically employed in technological applications, the formation of thin films by using electrosynthesis directly onto conductive substrates has been scarcely investigated [10, 11].

Since there is a great interest in the characterization of carbene structures to produce low-cost semiconductor thin films, in this work we studied the influence of the preparation technique, the type of substrate employed and the addition of a bidentate ligand on the morphological and conductive properties of Fischer carbenes thin films. A simple method has been developed to synthesize a molecular semiconductor from the chemical reaction of derivatives of Tetracarbonyl ((Z)-(2-Methyl-3-(Methylate)-3-(Phenyl- $\kappa$ -imin)-1-(Pirrolidin-1-il) Propiliden)) Tungsten 0 ( $C_{19}H_{20}N_2O_4SW$ ) and bidentate amines. This paper reports on the synthesis and characterization of thin films that were formed through an oxidation–reduction reaction in an electrosynthesis cell from electronic acceptor and donor species. Material characterization was made through infrared (IR) spectroscopy and energy-dispersive spectroscopy (EDS). Thin films were electroplated, in the electrochemical module of the atomic force microscopy (AFM) and the electrical conductivity was measured at different temperatures in order to evaluate the conductivity behavior of these compounds. After the synthesis and characterization, a comparative study was made between these materials and their relation to the highly ordered structure and marked anisotropy that generates a preferential direction for the electric charge transport.

## 2 Experimental procedure

High purity raw materials were obtained from commercial suppliers with no further purification. The synthesis of  $C_{19}H_{20}N_2O_4SW$  was followed according to Cedillo et al. [12] from the reaction between the pentacarbonyl ((pirrolidin-1-il) tungsten(0), in front of the aryl isothiocyanate. Vibrational spectra were obtained with a Perkin Elmer IR spectrophotometer model 282-B, using KBr pellets.

0.06 grams (0.1 mmol) of  $C_{19}H_{20}N_2O_4SW$  are added to 0.01 g (0.1 mmol) of 1,4-diaminobutane (**Compound A**) or 0.1 g (0.4 mmol) of 2,6-diaminoanthraquinone (**Compound B**) and dissolved in 20 ml of ethanol. Keep in reflux for 72 h. The solid was filtered off, washed with absolute ethanol and vacuum-dried. The product was recrystallized in a 1:1 ethanol–water solution.

### 2.1 Compound A ( $C_{23}H_{30}N_3O_4SW$ )

Yield reaction 56 %. IR (KBr pellet,  $cm^{-1}$ )  $\nu_{max}$ : 1,998, 1,867 (W–CO); 1,570 (N=C); 2,928 (NH<sub>2</sub>); 3,028 (N–H); IR (thin film,  $cm^{-1}$ )  $\nu_{max}$ : 1,999, 1,865 (W–CO); 1,573 (N=C); 2,925 (NH<sub>2</sub>); mp 210 °C. MS(FAB<sup>+</sup>, DMSO/EtOH)  $m/z$ : 628[ $C_{23}H_{30}N_3O_4SW$ ]<sup>+</sup>, 556[ $C_{19}H_{20}N_2O_4SW$ ]<sup>+</sup>, 528[ $C_{18}H_{20}N_2O_3SW$ ]<sup>+</sup>, 500[ $C_{17}H_{20}N_2O_2SW$ ]<sup>+</sup>, 472[ $C_{16}H_{20}N_2OSW$ ]<sup>+</sup>, 444[ $C_{15}H_{20}N_2SW$ ]<sup>+</sup>.

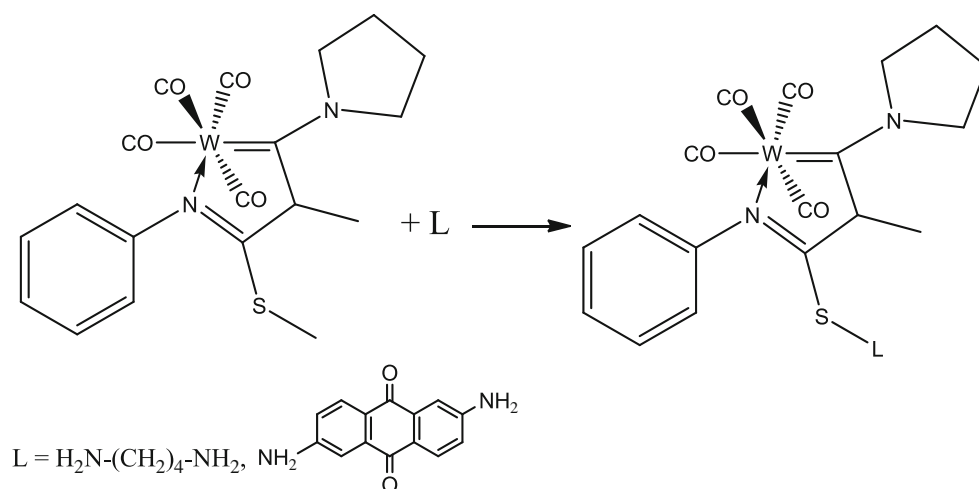
### 2.2 Compound B ( $C_{33}H_{28}N_3O_6SW$ )

Yield reaction 55 %. IR (KBr pellet,  $cm^{-1}$ )  $\nu_{max}$ : 1,998, 1,864 (W–CO); 1,570 (N=C); 3,422 (NH<sub>2</sub>); 3,068 (N–H); 1,658 (C=O); IR (thin film,  $cm^{-1}$ )  $\nu_{max}$ : 2,000, 1,865 (W–CO); 1,573 (N=C); 3,425 (NH<sub>2</sub>); 1,655 (C=O); mp 240 °C. MS(FAB<sup>+</sup>, DMSO/EtOH)  $m/z$ : 778[ $C_{33}H_{28}N_3O_6SW$ ]<sup>+</sup>, 556[ $C_{19}H_{20}N_2O_4SW$ ]<sup>+</sup>, 528[ $C_{18}H_{20}N_2O_3SW$ ]<sup>+</sup>, 500[ $C_{17}H_{20}N_2O_2SW$ ]<sup>+</sup>, 472[ $C_{16}H_{20}N_2OSW$ ]<sup>+</sup>, 444[ $C_{15}H_{20}N_2SW$ ]<sup>+</sup>.

The synthesis procedure used is as per the following: Starting from the precursor sample in order to obtain *compounds A* and *B* as schematically shown in Fig. 1. The condensation reaction implies the subtraction of a hydrogen, with the formation of the correspondent anion, stabilized by the relocation in the metallic fragment, united to an electrophilic addition. As for IR spectroscopy, the synthesized materials show bands relating to the sign of the metallic carbonyls at 1,998–2,000 and 1,864–1,867  $cm^{-1}$ . The above mentioned indicate a major electronic donation to the tungsten atom, due to the coordination of the heteroatom. On the other hand, the band corresponding to the  $\nu(N=C)$  vibrations at 1,570–1,573  $cm^{-1}$ , related to the Fischer carbene, and the band, due to  $\nu(NH_2)$  vibrations of the amine bounded to the Fischer carbene occurring at 2,925–3,425  $cm^{-1}$ , are present as well. Finally, the *compound B* gives rise to the  $\nu(C=O)$  band in the range of 1,655–1,658  $cm^{-1}$  corresponding to the anthraquinone from the 2,6-diaminoanthraquinone. Despite the relatively low solubility of the obtained powder compounds, the positive-ion FAB mass spectra have shown signals for  $m/z$  628 and  $m/z$  778 confirming the presence of the acceptor and donor compounds. The molecular ion  $m/z$  556 is also present, confirming the coordination of the heteroatom and the peaks  $m/z$  528, 500, 472 and 444, obtained by the successive loss of the four metallic carbonyls.

The initial stages of electrochemical deposition by using the AFM surface characterization were carried out in situ in the electrochemical (EC) fluid cell of an atomic force microscope, Nanoscope IIIa Digital Instrument. Here, highly oriented pyrolytic graphite (HOPG) was used as a working electrode, platinum wire as a counter electrode and silver wire as a reference electrode. For this study, 0.1 M

**Fig. 1** Chemical structures of the synthesized molecular materials, obtained from Fischer carbenes compounds (*L* represents the bidentate amine)



tetrabutylammonium tetrafluoroborate was used as support electrolyte and the Tetracarbonyl complexes were dissolved in absolute ethanol with a 0.01 M concentration. The AFM characterization of the electrodeposited material was performed in the presence of the aqueous electrolyte (50  $\mu\text{l}$ ). In order to compare the electrode surface modification before and after deposition, the HOPG was imaged before the electrochemical reactions and after different potential scan cycles (PSC). The use of AFM for the electrodeposition of thin films allows studying the reduction–oxidation electrochemical processes occurring in the cell, with the aid of an electrochemical module (potentiostat/galvanostat). Scanning electron microscopy (SEM) was carried out in a Leica Cambridge, Stereoscan 440 model with a coupled microanalysis system including X-ray Energy Dispersive Spectrometer (EDS). Finally, the electric conductivity of the films was studied by means of a four-point probe; for these measurements, the molecular films onto the HOPG substrates were analyzed by using four metallic strips acting as electrodes for the electrical measurements. The electric current as a function of temperature was measured with a 100 V applied voltage in the ohmic regime by using a Keithley 230 programmable voltage source and a Keithley 485 peak-ammeter coupled to an HP3421 data collector.

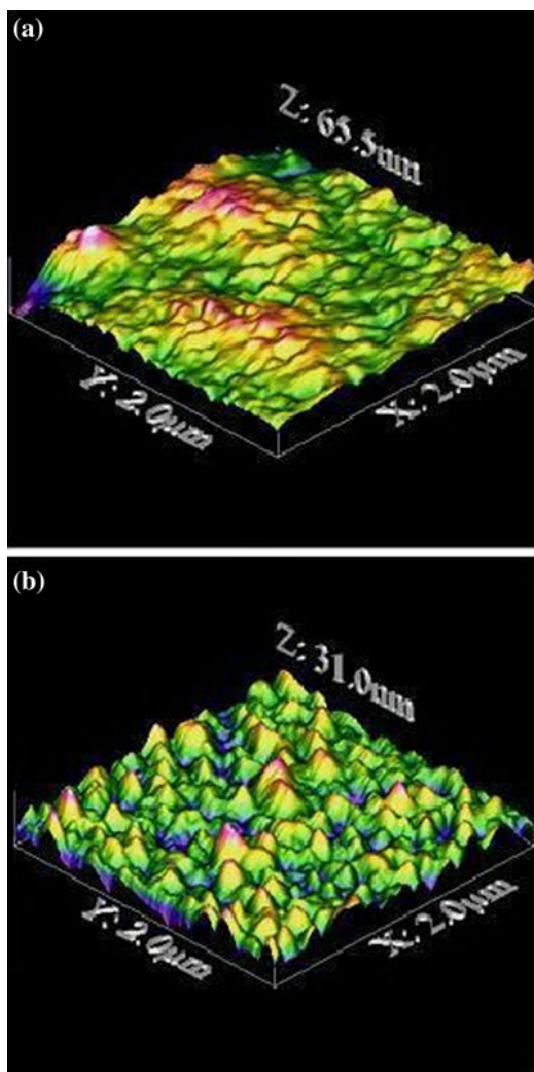
### 3 Results and discussion

Electrosynthesis is the process for synthesizing molecular materials which provides the best results, and is based on the formation of the radical ion by electrochemical oxidation or reduction and the simultaneous crystallization of the derived salt with the inorganic counter-ion of the supporting electrolyte. In this study, the electrochemical reaction in the AFM permits the formation of a thin film over an electrode surface shaped as a plate or a disk. This constitutes the main reason why the deposited film acquires

this morphology and allows evaluating the electrical properties of the molecular material. Figure 2 shows the AFM images of the deposited thin films. From these images, it is clear that the film surface changed dramatically depending upon the starting material. Notwithstanding the effort to keep the parameter deposition constant, the differences on the films' surface may be due to a variation in the bidentate amine in each molecular material. The root mean square (r.m.s.) roughnesses evaluated from the AFM measurements of the thin films is 73.6 and 47.4  $\text{\AA}$ , for  $\text{C}_{23}\text{H}_{30}\text{N}_3\text{O}_4\text{SW}$  and  $\text{C}_{33}\text{H}_{28}\text{N}_3\text{O}_6\text{SW}$  respectively.

The energy dispersive spectroscopy (EDS) analysis was made for molecular materials synthesized as powder and thin film. The results for  $\text{C}_{23}\text{H}_{30}\text{N}_3\text{O}_4\text{SW}$  powder and thin film may be observed in the Fig. 3a, b.  $\text{C}_{23}\text{H}_{30}\text{N}_3\text{O}_4\text{SW}$  was synthesized from the inorganic compound  $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_4\text{SW}$  and from the 1,4-diaminebutane. As observed in Fig. 3, the presence of O, S, W which belong to the anionic part of material, these results confirm the fact that during the electroplate, no chemical change of material, was performed. Similar results were obtained for material synthesized from 2,6-diamineanthraquinone. These results are complemented with those obtained through IR spectroscopy (see “Experimental procedure”), the deposited films are formed by the same macro-ions as those of the original synthesized powder, as indicated by comparison between the locations of the absorption bands in the spectra of the synthesized powders and those of the deposited films.

In order to investigate the electrical behavior of the synthesized materials, the variation of electrical conductivity with temperature in thin films was evaluated. Figure 4 shows the variations in electric conductivity with increasing temperature, through thin films made of each synthesized molecular material. For both molecular materials, the observed curves suggest a semiconductor-like behavior. The variation is linear indicating the presence of only one type of conduction mechanism. The variations observed in the magnitude of electric conductivity may be due to the different amine groups.



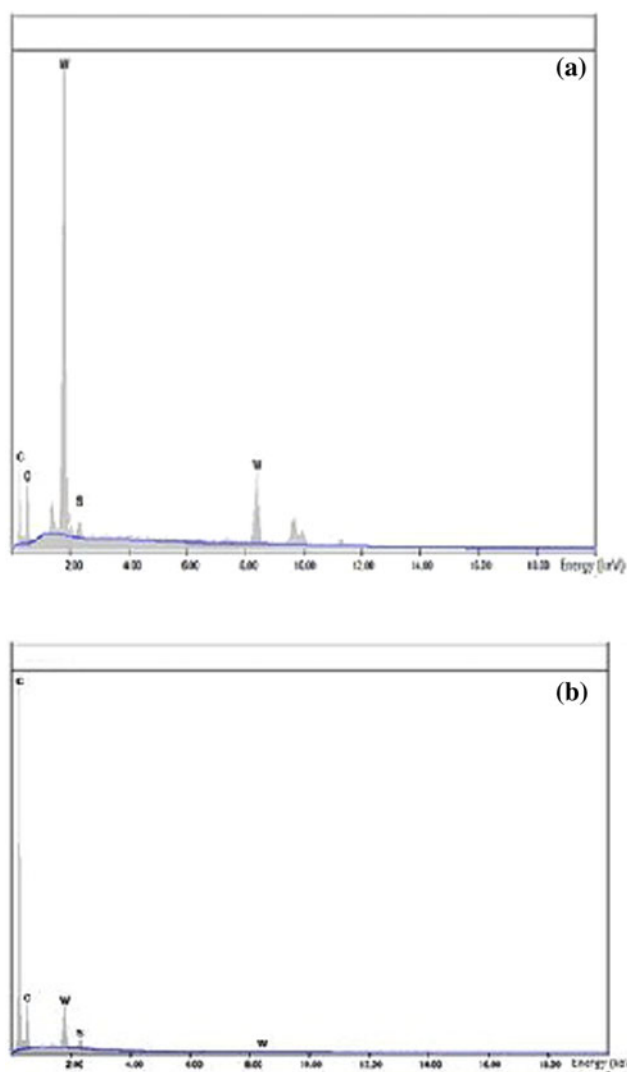
**Fig. 2** 3D AFM micrograph of thin films **a**  $C_{23}H_{30}N_3O_4SW$  and **b**  $C_{33}H_{28}N_3O_6SW$

In these materials, compounds with voluminous substitutes and high molecular weights such as 2,6-diamineanthraquinone ( $C_{33}H_{28}N_3O_6SW$ ), present the largest conductivity. The electrical conductivity of each material was evaluated at 25 °C with the results shown in Table 1. The thin films practically behaved as insulators at room temperature, however, their conductivities increased as the temperature increases, indicating semiconducting behavior.

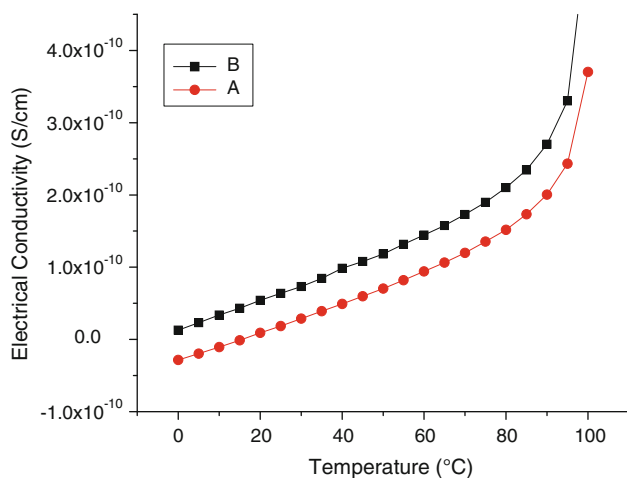
The electric conductivity  $\sigma$  of these materials depends on the absolute temperature  $T$  as described by Eq. 1:

$$\sigma = \sigma_m \exp\left(-\frac{\Delta E_m}{KT}\right) \tag{1}$$

where  $\sigma_m$  is the pre-exponential factor,  $\Delta E_m$  is the activation energy for electric conductivity, and  $K$  is the Boltzmann constant. The quantity  $\Delta E_m$  is an activation energy involving both the energy necessary to excite



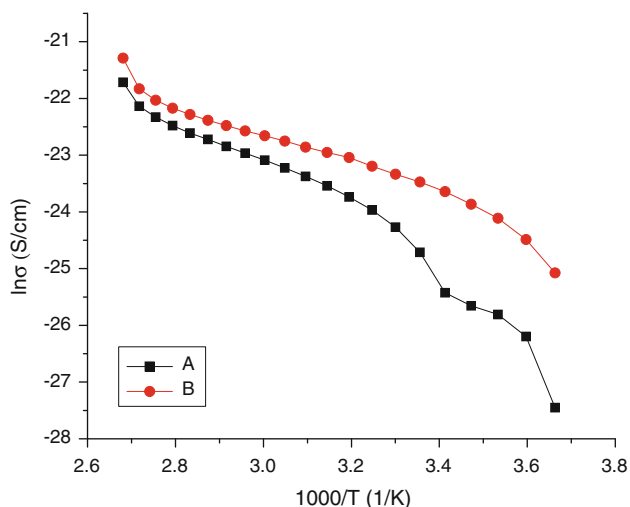
**Fig. 3** EDS measurements for  $C_{23}H_{30}N_3O_4SW$  in **a** powder and **b** thin films



**Fig. 4** Electrical conductivity variation through the films as function of temperature for (A)  $C_{23}H_{30}N_3O_4SW$  and (B)  $C_{33}H_{28}N_3O_6SW$

**Table 1** Electrical conductivity ( $\sigma$ ) and activation energy of electrical conduction ( $\Delta E_m$ ) for thin-film samples

Compound	$\sigma_{298\text{ K}}$ ( $\text{S cm}^{-1}$ )	$\Delta E_m$ 1 (eV)	$\Delta E_m$ 2 (eV)
$C_{23}H_{30}N_3O_4SW$	$1.85 \times 10^{-11}$	1.82	0.55
$C_{33}H_{28}N_3O_6SW$	$6.39 \times 10^{-11}$	1.4	0.4

**Fig. 5** Temperature dependence of the electrical conductivity of materials (A)  $C_{23}H_{30}N_3O_4SW$  and (B)  $C_{33}H_{28}N_3O_6SW$ 

electrons from the localized states toward extended states through the mobility edge and the electrical conduction by means of the hopping mechanism between localized states. A plot of  $\ln \sigma$  versus  $1,000/T$  yields a straight line whose slope can be used to determine the thermal activation energies of the complexes [13]. As can be seen in Fig. 5, the curves are characterized by two regions with different slopes associated to intramolecular and intermolecular conductivity. The calculated activation energies are shown in Table 1 with the higher values related to the intramolecular conduction process. In intermolecular transfer, electrons can hop from one atomic site to another if orbitals exist at these sites with the same energy levels. The intramolecular conduction process occurs between the metal atom and the ligands in the complex [13]. This is because the carbene in these materials behaves as a neutral ligand, donating a pair of electrons. The carbene–tungsten link consists of a  $\sigma$ -bond between the free electrons of the carbon atom and a  $d$  empty orbital of the metal, and by the  $\pi$ -donation between a  $d$  full orbital of metal, to a  $p$  empty orbital of the carbon atom (retro-donation). The heteroatom may also donate electronic density to the carbon atom, through the interaction between  $p$  orbitals [12].

In the case of intermolecular orbital overlap, electrons or holes can travel from one kind of macromolecule to another [13]. These structures present preferential directions for electric conduction via the amine that lead to a remarkable anisotropic character, which is why they have been called

“pseudo-one-dimensional” materials.  $\pi$ -electrons can also move from one type of macromolecule to another by hopping if orbitals with the same energy levels exist between the complex molecules. Therefore according to Sarkar et al., the first step of conduction starts between molecules, but both processes should be considered. The intramolecular conduction process occurs between the metal atom and the ligands and the intermolecular conduction process between two macromolecular complexes [13].

## 4 Conclusions

New semiconductor materials from  $C_{19}H_{20}N_2O_4SW$  and bidentate amines were synthesized. Thin films have been electrodeposited in the electro-crystallization module of the AFM. Although the deposited material is amorphous in nature, it is formed by the same chemical units as the synthesized powder. The films show semiconducting characteristics. The electron transport is strongly influenced by their molecular structures: the amine is the factor that determines the electrical conductivity of a material.

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