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The effect of the double doping on the electrical properties of polyaniline

Hisham A. Saleh [a], Huda A. Younis [b*]

[a] *Collage of Education, University of Mosul,Mosul,Iraq*

[b*] *Technical Institute –Mosul, Northern Technical University, Mosul,Iraq*

Abstract

The research included a study of the effect of double doping on the electrical conductivity of polyaniline (PANI) after it was prepared by pure aniline polymerization (oxidation polymerization) as a first step, and then doping the polyaniline by monomeric doping with acid solutions of each of the two acids H_2SO_4 and HCl with different concentrations each separately, then doping Polyaniline monomeric doping with chloride salt ($FeCl_3$, $HgCl_2$, $CuCl_2$, AgCl) with different weight ratios. The acidic doped polyaniline was doped again with salt, the third step, it is the process of double doping of a polymer using acids and metal salts together. As this process is done by doping the polymer with sulfuric acid at a concentration of (1M) (which gave the highest electrical conductivity), and then re-doping this acid-stained doped form using the metal salt ($HgCl_2$) (which gave the highest electrical conductivity among other ionic dopants) and by weight ratios% (3, 5, 10, 15, 20). The characteristics of (I-V) were measured to show the mechanism of electrical conduction in the polymer using an electrical circuit manufactured locally in the laboratory and by applying different efforts, as the results were shown. The double doping has a clear effect on the electrical conductivity, and it is higher than the electrical conductivity of the un-dopped and monomeric models with acid solutions or metal salts.

Keywords: Doping Process, Polyaniline, Electrical Properties, double doping

1. Introduction

Most polymers are insulating materials, while polymers with successive structures have semiconductor properties.

Due to the ease of forming polymers, chemists and physicists began since the eighties of the nineteenth century with studies aimed at developing electrically conductive polymers (successive), containing an extension of electrons along the polymeric chain [1]. where the electrical conductivity values of semiconductors range between (10^{-8}–10^{-3}) $S.cm^{-1}$ [2], and it is much larger than insulating materials and lesser than metals.

Scientists have focused on successive polymers in their quest to develop polymers with high electrical conductivity characteristics, The prevailing belief was that the delocalization of electrons that is supposed to happen in these polymers is necessary to give a high concentration of charge carriers that carry the current, but the scientific results clearly showed that the delocalization of electrons along the chain is not sufficient to make these polymers have high conductivity where they are at best weak semiconductors, this is because the electron transfer process takes place within a single chain, meaning that the electronic sequence is cut off at the end of the chains, but charges that have mobility can be generated, either by shining light, shedding an electric voltage, or introducing chemicals called dopants and by the process of doping, which has a great role in giving off a high concentration of charge carriers that transmit electric current [3, 4,5].

There are many studies that have been concerned with the electrical properties of polymers and the effect of monomeric doping of various kinds on them [6,7,8,9].

Polyaniline is one of the family of successive polymers. and it is semi-flexible rod polymer [10], and it has a number of important properties and applications [11,12,13]:

It has high thermal stability (within the preparation environment), as its melting point is 307°C, it has high elastic mechanical properties, has

*Corresponding author e-mail: hudaa.younis@ntu.edu.iq

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distinctive electrical and optical efficiency, has a clear response to the oxidation and reduction processes that occur after the deformation process, and easy preparation as well as the doping process, in addition to the fact that most of its practical applications are in the fields of electronics, sensors, and the manufacture of light-emitting diode and transistor. One of the most important of these applications is that it is used in the manufacture of electronic cards with an electronic footprint.

1.1. **The aim of the research**

Most of the studies that have been performed on conductive polymers are the study of the electrical properties of monomeric doping polymers, and there are no studies indicating the use of the idea of double doping. Therefore, the aim of the research was to study the effect of double doping on the electrical properties of (I-V) and electrical conductivity of the polyaniline.

2. Experimental

2.1. the preparation of polyaniline:

The polyaniline was prepared by oxidation polymerization (aniline oxidation) [14] .

Where 15 ml of pure aniline is dissolved in 600 ml of (1M) hydrochloric acid solution, in a reaction flask with cooling to 5°C, then a solution of ammonium persulfate (28.2 g) dissolved in 300 ml of (1M) hydrochloric acid is added to the The reaction flask was dropwise for 15 minutes, using a separating funnel with constant stirring. Two hours after the start of the reaction, the formed precipitate is filtered, and the precipitate is washed well using 100 ml of (1M) hydrochloric acid solution. Then it is left to dry at laboratory temperature for 48 hours . the precipitate formed is in the form of fine green crystals of polyaniline doped with hydrochloric acid.

To obtain the basic (undoped) polyaniline: Take 5 g of the prepared polyaniline dissolved in 500 ml of a solution (0.1 M) of ammonium hydroxide with continuous stirring for 3 hours and at laboratory temperature. Then we filtered and dried the precipitate to obtain blue crystals of undoped polyaniline. figure (1).

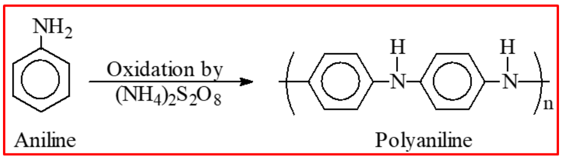

Figure 1: Scheme of polymerization of aniline

The infrared absorption spectrum (using a WQF-510 infrared device) of this polymer showed a clear beam at the frequency of 3550 cm-caused by the expansion of the NH bond, and another beam located between the frequencies (750-850) cm-confirms the compensation at the Para site on the aromatic ring.

2.2. the process of doping the polymer (PANI):

2.2.1. the process of monomeric doping :

Two methods of doping on polymer (PANI) were performed as follows:

First :Doping by acidic solution :

The polymer is dopped by exposing it to solutions of acids (HCl, H_2SO_4) with different molar concentrations of (0.25, 0.5, 0.75, 1) M for 24 hours, then the deformed polymer is filtered, dried and pressed.

Second : Doping by mixing :

This process is carried out by direct mixing of the polymer with the dopant, by taking a certain weight of the polymer and mixing it with the impurity in specific weight ratios (3%, 5%, 10%, 15%, 20%), and here the two materials (polymer and the dopant) are thoroughly grinded using a special mill for this purpose and they are mixed for a long time in order to evenly distribute the dopant between the polymer chains. This method is widely used in case of using salt as a dopants.

2.2.2. The process of double doping

It is done by taking the sample of the polyaniline that was monomerically dopped with the acidic solution H_2SO_4, which gave the highest conductivity at 1M concentration, and then it was doped(double doping) by mixing it with different weight ratios of the $HgCl_2$ dopant, with the commitment to obtain the required sample weight.

2.3. Preparing the samples

The pure and dopped PANI models were pressed by a (GH) press of Turkish origin with a maximum compressive strength equal to (4570Psi) equivalent to (315bar), in the form of circular discs with a surface area ($2cm^2$) and thickness ranging between (0.8-1) mm using Homemade steel mold at laboratory temperature.

2.4. The method of measuring the electrical conductivity [15,16]

The characteristics of (I-V) for the polyaniline samples were studied using the electrical circuit shown in Fig. (2), by shedding the potential difference (90-6000) V.

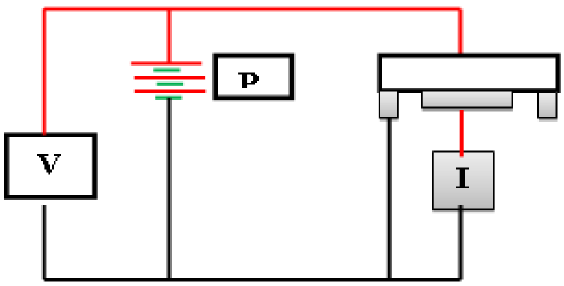

Figure 2 : Electrical circuit for volumetric conductivity measurement

The volumetric electrical conductivity of the models is calculated according to the following equation [17,18]:

$$\sigma = I \times d / V \times A \quad \text{........ (1)}$$

σ = volumetric conductivity ($S.m^{-1}$),
I = the current running through the modules (Amp)
V= potential imposed (Volt),
d = the thickness of the model used in unit (m)
A= the surface area of the model in unit (m^2)

2.5. Infrared Spectroscopy (FT-IR)

Infrared spectroscopy was used to study the particle structure of the prepared models, by KBr method by using the infrared spectroscopy (FT-IR) type WQF-510 English origin as we mentioned earlier.

3. Results and Discussion

3.1. pure state

The process of determining the mechanism of electrical conduction depends mainly on the study of the characteristics of (current - voltage), it has been noted that the relationship between current and voltage is not linear, but rather follows the law of forces ($I \propto V^m$), and in order to determine the mechanism of electrical conduction, the relationship between the logarithm of current and the logarithm of voltage was drawn. Figure (3) shows the (Log I - Log V) properties of pure polyaniline at laboratory temperature, as we notice from the figure that the current increases with increasing voltage and for the voltage ranges from (90-6000 volt).

The behavior of pure polyaniline is Ohmic behavior, and the relationship between current and voltage is a straight line has a slope that represents the value m is equal to one within the range of low voltages. We also note that the value of m is approximately equal to two within the range of medium and high voltages, that is, the behavior of pure polyaniline within these ranges is the current determined by the charge of the vacuum.

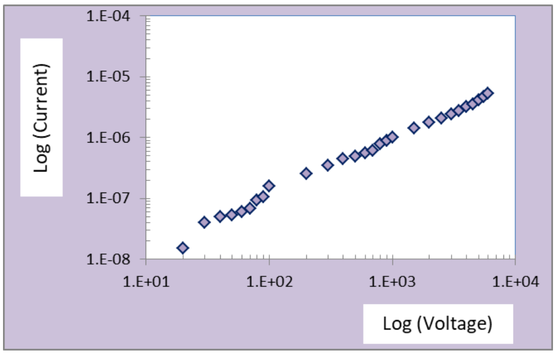

Figure 3 : Logarithmic relationship between current and voltages for pure polyaniline

3.2. Doping process

3.2.1. Single doping

By single doping, it means the use of one type of dopants and in a way that suits the type of that dopant, as follows:

First: doping with an acidic solution (H_2SO_4, HCl):

Doping with acids is very effective with successive polymers, especially those that contain nitrogen in their composition, such as polyaniline [19].

Figures (4 and 5) show the increase in the electrical conductivity (σ) of the doped polymer by increasing the molar concentration of the acids, as the highest conductivity was at the concentration (1M) for both acids. This increase is attributed to the so-called proton exchange (which is the high ability of acidic protons to transfer from one molecule to another) and this characteristic makes acids good protonic dopants for successive polymers.

However, H_2SO_4 acid solutions had a stronger effect than the proton ions of HCl acid solutions. The reason for this is that H_2SO_4 acid has a high ability to improve the conductivity of the polymer through the protonation process (the proton transfer of a hydrogen molecule from one molecule to another through the polymeric chain). The acid is in a state of constant movement and with the increase in the molar concentration of the acid, the proton ions (impurities) increase and in this way the protons work to transfer electric current due to the applied voltage from one polymeric chain to another.

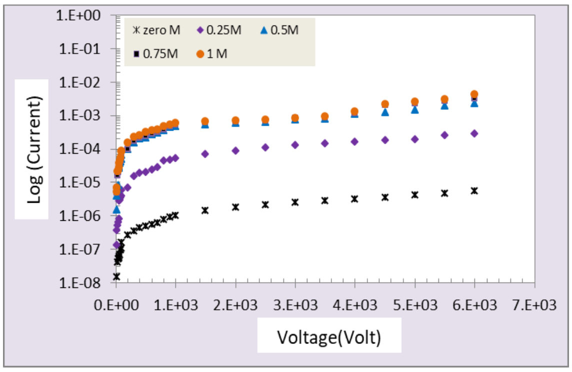

Figure 4 : Characteristics of (Log I-V) for single dopped polyaniline with different concentrations from HCl acid

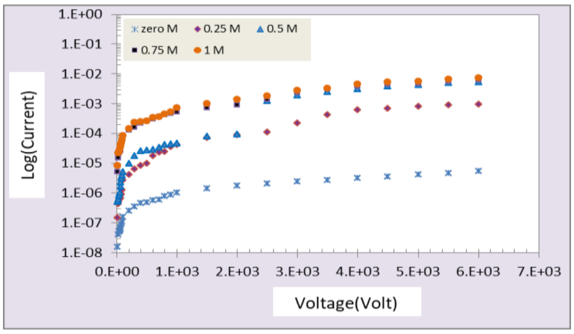

Figure 5 : Characteristics of (Log I-V) for single dopped polyaniline with different concentrations of H_2SO_4 acid

We note from Table (1) and Figure (6) the electrical conductivity of polyaniline with the change in the concentration of the dopant, where the higher the concentration of the dopant , the higher the electrical conductivity of the polymer. The conductivity of polyaniline dopped with acid (H_2SO_4) at the concentration (1M) was enhanced by three orger of magnitude than the conductivity of pure polymer. The electrical conductivity of polyaniline doped with sulfuric acid is better than that of polyaniline doped with hydrochloric acid.

Table 1: The electrical conductivity values of the denatured polyaniline with different concentrations of (H_2SO_4, HCl)

Elecitrical conductivity (S/Cm)		Molarity (M)
H_2SO_4	HCl	
6.10E-11	6.10E-11	0.0
5.16E-09	3.92E-09	0.25
7.30E-08	8.01E-09	0.5
1.50E-07	4.65E-08	0.75
4.22E-07	7.80E-08	1.0

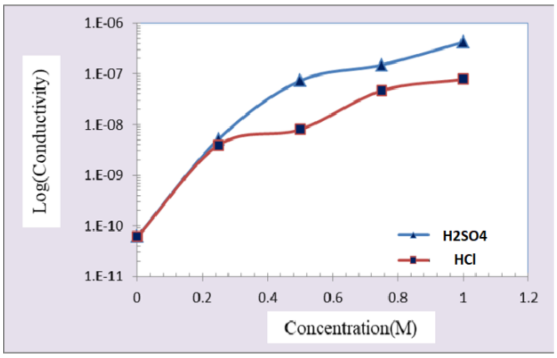

Figure 6 : The electrical conductivity relationship of single dopped polyaniline with molar concentrations (H2SO4, HCl)

3.2.2. Single doping with metal chlorides (ionic dopants)

Metal chlorides ($FeCl_3$, $HgCl_2$, AgCl, $CuCl_2$) were used as ionic dopants for polyaniline, and the results showed changes in the electrical conductivity of this polymer after doping.

Figures (7,8,9,10) show the increase in current by increasing the voltage applied to polyaniline doped with metal chlorides at laboratory temperature.

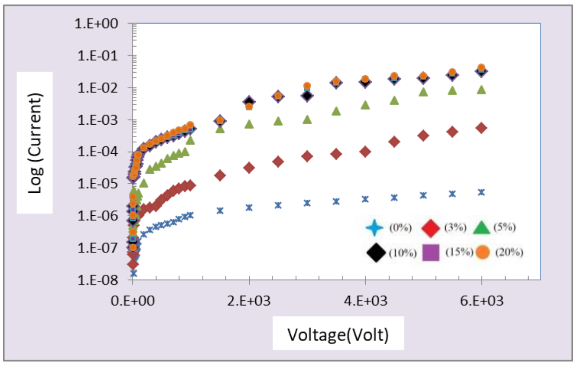

Figure 7: Characteristics of (Log I-V) for single-dopped polyaniline with different weight ratios of CuCl2

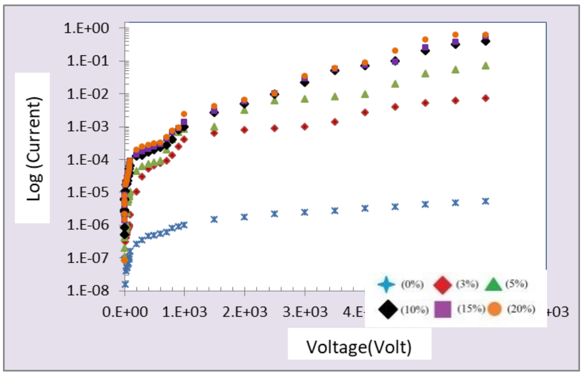

Figure 8 : Characteristics of (Log I-V) for single dopped polyaniline with different weight ratios from AgCl

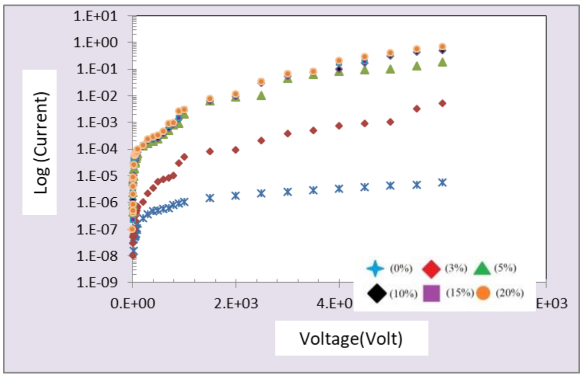

Figure 9: Characteristics of (Log I-V) for single dopped polyaniline with different weight ratios from $FeCl_3$

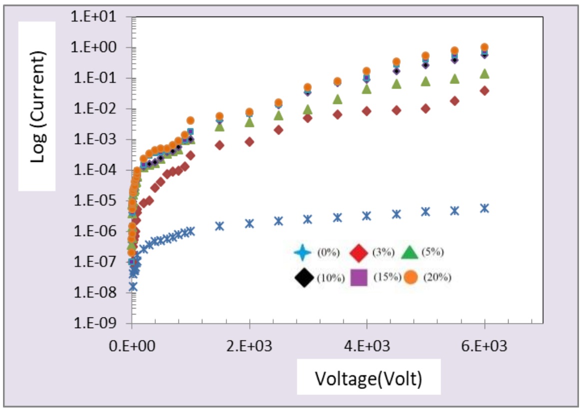

Figure 10: Characteristics of (Log I-V) for single-dopped polyaniline with different weight ratios of $HgCl_2$

The increase in current with an increase in the voltage applied to the polymer shows the improvement in electrical conductivity, which appears clear in Figure (11) which shows the relationship between electrical conductivity and the different weight ratios of ionic dopants.

As we also note in Figure (11) and Table (2), that the doped mercury chloride ($HgCl_2$) gave a clear improvement in the electrical conductivity, the conductivity increase was by (106) than the conductivity of the undoped polymer. As well as the increase in the electrical conductivity of polyaniline doped with ferric chloride and silver chloride by about the same amount, but slightly less than the electrical conductivity of polymer doped with mercury chloride.

In relation to the results obtained, the metal chlorides used in our research can be considered good dopants, because all these positive metal ions have empty orbitals in their outer shell, making them good electron-acceptors, while polymers are electron-donor units, because it contains pi (π) electrons in the aromatic ring, as well as this polymer contains the asymmetric electron pair on nitrogen atoms, which facilitates the process of forming complexes of the type (donor - acceptor) electronic, and this will certainly affect and effectively the process of charge transfer between the polymer and the doped [20,21,22].

Table 2: The values of electrical conductivity for polyaniline with different ratios of ($CuCl_2$, AgCl, $HgCl_2$, $FeCl_3$)

Percentage (%)	σ (S/Cm)			
	$CuCl_2$	$AgCl_2$	$FeCl_3$	$HgCl_2$
0	6.10E-11	6.10E-11	6.10E-11	6.10E-11
3	7.20E-09	7.48E-09	1.75E-08	7.00E-8
5	7.50E-08	8.50E-08	1.88E-07	2.73E-7
10	8.20E-08	8.75E-07	2.25E-06	2.61E-6
15	1.03E-07	1.86E-06	2.33E-06	2.93E-5
20	1.13E-06	7.40E-06	1.25E-05	2.15E-4

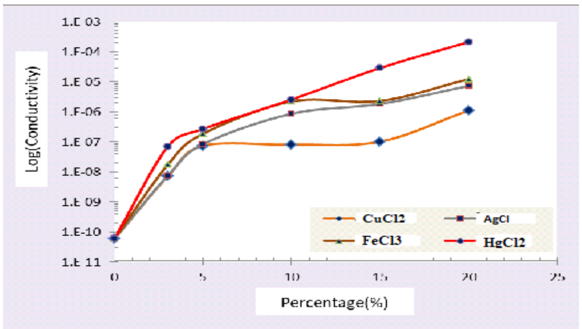

Figure 11: The effect of different weight ratios of ionic dopants ($CuCl_2$, AgCl, $FeCl_3$, $HgCl_2$) on the electrical conductivity of the polyaniline.

3.2.3. Double doping

After doping polyaniline with two types of acids (HCl,H_2SO_4), the results showed that the conductivity of polyaniline improved by about five order of magnitude after doping, and that sulfuric acid was the best acidic dopant , and that the best conductivity was at the concentration (1M). Then, these samples (polymer doped with (1M) of sulfuric acid) were mixed with different weight percentages of mercury chloride (as it gave the best improvement in the electrical conductivity of the polymer compared to the rest of the salts used in this research).

Table (3) and Figure (12) show the effect of double doping with mercury chloride (in different weight percentages) and sulfuric acid (1M concentration) at laboratory temperature.

Table 3: The electrical conductivity values of PANI bilayer doped by [(1MH_2SO_4 + $HgCl_2$ (0-20%)]

	weight ratio of ($HgCl_2$)	σ(S/cm)
PANI doped with (1M H_2SO_4+$HgCl_2$) at R.T	Pure PANI	6.10E-11
	0%	1.50E-5
	3%	2.33E-05
	5%	3.68E-05
	10%	7.35E-04
	15%	3.06E-03
	20%	1.16E-02

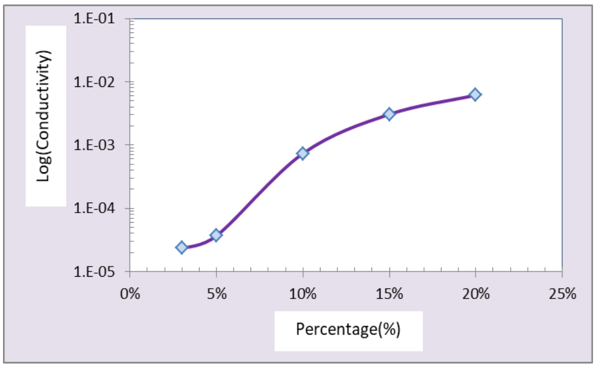

Figure 12 : The electrical conductivity (σ) of the double doped polyaniline with [1 M H2SO4 + HgCl2 (3-20)%]

Figure (13) shows the difference in the improvement of the electrical conductivity of single and double doped polyaniline and the pure state. we note the obvious increase in electrical conductivity after double doping, which was 100 million times greater than that of pure polyaniline.

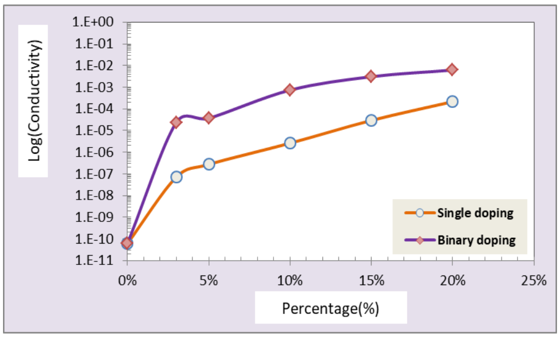

Figure 13: The deference of electrical conductivity of the (single & binary) doped polyanilin with different weight ratios of $HgCl_2$

The increase in the electrical conductivity of the double-doped polymers (using H_2SO_4 and $HgCl_2$) is an increase in the electronic density around the active groups in the polymer, as well as the increase in the delocalization and stability of the electrons (resonance state), and an increase in electronic affinity which in turn leads to an increase in the concentration of charge carriers and thus an increase in the electrical conductivity of the polymer.

4. Conflicts of interest

There are no conflicts to be reported

5. Acknowledgments

I extend my heartfelt thanks to all professors and colleagues who helped me complete the laboratory tests for the research, and I also extend my gratitude to those who helped me write the research.

6. Conclusions

1- The strength of the acid and the ability of the polymer to protonation are the two main factors affecting the electrical conductivity of acid-dopped polymer .
2- The acid solution H_2SO_4 was more effective than the acid solution HCl in increasing the electrical conductivity of polyaniline, and $HgCl_2$ was more effective than the rest of the metal salts that were used.
3- Metal chlorides (especially those used in our research) are good dopants, because all these metal ions have empty orbitals in their outer shell, which makes them good electron acceptors that can form complexes of a special kind with the active groups in the polymer , and these complexes effectively affect the charge transfer process.
4- The best electrical conductivity of the polyaniline (1.16E-02) can be obtained using the double doping method.
5- The enhancement of the electrical conductivity of the polyaniline reached 10^{-2} $S.cm^{-1}$,we highly recommend to use these composites to be used in semiconductor purpose.

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