Carbon Nanotubes Ammonia Sensor Printed by Aerosol Jet System

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Summary: This article deals with ammonia gas sensor based on carbon nanotubes. Active layer is deposited on a flexible substrate by new deposition technique called Aerosol Jet. The deposition technique remove deficiency of today's common used deposition technique where is very difficult to deposit a thin homogeneous layer of carbon nanotubes. The final sensor was tested against to 50 ppm ammonia concentration at the room temperature. The electric parameter changes of the sensor during the testing was measured by AC LRC bridge and achieved results are discussed.

Key words: Aerosol Jet System, carbon nanotubes, gas sensor, printed electronic

Introduction

Flexible electronics (FE) is a relatively new discipline and many scientific teams have been focusing on this branch of electronics. The aim of this field is not to replace common silicone-based components but to fill the gap where the classical components cannot be used, for example, electronic parts that are mechanically stressed. At present, there are a lot of activities to prepare flexible devices such as transistors, photodetectors, switches, etc., because of many application possibilities for their use. Printed sensors represent the big field for many of these applications. They have great potential for special application such as fully printed electrical circuits, smart textile, smart labels and generally at the internet of things (IoT)[1],[2].

Nowadays, carbon nanotubes (CNT) are deeply investigated in many applications due to their exceptional properties. One of them is a huge surface whose value reaches over 1000 m2/g [3]. This is the reason why carbon nanotubes are good candidates for their use as an active layer in gas sensors development. Their enormous surface represents a lot of space for the interaction of gas molecules. Sensor properties are determined by a sensor active layer. The homogeneity of this layer is key to achieve the highest sensitivity and also affects the other properties of the sensor, therefore, the emphasis on deposition is very high. There is a big problem at thin films deposition of CNT by conventional deposition techniques (dip coating, drop coating, spin coating etc.) because the used solvent evaporate very slowly. Due to it the "coffee rings" are created during the layer forming. That leads to carbon nanotube agglomeration[4]. The methods that can achieve very thin layers are suitable, not only because of the high conductivity of carbon nanotubes but also because of the efficient and fast charge transfer from the surface of the layer towards to electrodes. A more efficient charge transfer results in a faster sensor response. We used special and quite new printing technique for the creation of thin and homogenous layer from carbon nanotube dispersion on flexible substrate, called Aerosol Jet System (AJS).

Materials and experiments

The sensor is composed of three parts, namely: substrate, interdigital electrodes (IDE) and the active layer. The electrodes and active layer are printed by Aerosol Jet System on polyimide substrate. Polyimide is used as substrate due to its temperature and chemical resistance. The temperature resistance is up to 350 °C. Platinum nanoparticles and carbon nanotubes are convert to liquid phase by using various solvents which can etch surface of the substrate. That is the reson why the polyimide was used. The IDE are made of platinum ink purchased from Fraunhofer IKTS. The printed platinum interdigital electrodes are annealed at the 140 °C for 15 minutes. These values are sufficient to bring the nanoparticles together and the electrodes reach the required conductivity. The IDE are covered by thin layer of carbon nanotubes by the same deposition technique. The carbon nanotubes was obtained from Brewer Science. Water dispersion of these CNT contain 75% single wall carbon nanotubes (SWCNT) and 25% multi wall carbon nanotubes (MWCNT). The CNTs surface is covered by molecules of pyrene, where each molecule contains three SO_3H side groups for the better dispersion long-term stability.

The final sensors was exposed to ammonia and tested. The test was carried out under the room temperature (21 °C) and relative humidity 40 %. These condition should simulate a common working environment of the sensor. Ammonia concentration was set on 50 ppm during the sensor testing. This level of concentration follows the maximum exposure limit that cannot be exceeded to avoid harm of the human health. The electric properties of CNT sensors during the temperature testing was measured by AC LRC bridge – Agilent E4980 A. The main observed sensor parameter was its impedance.

Results and discussion

The Aerosol Jet System is a selective and additive deposition technique. That means the pattern is created directly on the substrate. Patterns are easily designed and modified by the CAD software. The principle of AJS is the aerosol creation from the special ink by external forces. There are two possibilities how to create the aerosol (Fig.1). The first possibility is a pneumatic atomizer and second one is ultrasonic atomizer. Ultrasonic atomizer was chosen for the deposition of both materials (CNT and platinum ink) because its advantage is that only very small amount of material is needed, approximately 1mililiter. This is very economical when expensive metals such as noble metals and carbon nanotubes are printed. Secondary effect of the ultrasonic atomizer is further break down of the agglomerates that may have formed. Ultrasonic source (frequency is 1.6 MHz) create a wave goes through liquid medium. Inside of this liquid is a submerged vial with the ink where the aerosol was created. The aerosol is transported from atomizer to the nozzle by nitrogen stream. The same medium is used for aerosol beam focusing at the nozzle output. Heating work surface where the substrate is attached, contributes to creation of the layer with required parameters. Small droplets of the aerosol combining with substrate heating leads to the creation of the very thin and homogeneous layer. Final sensor element is shown on Fig.2.

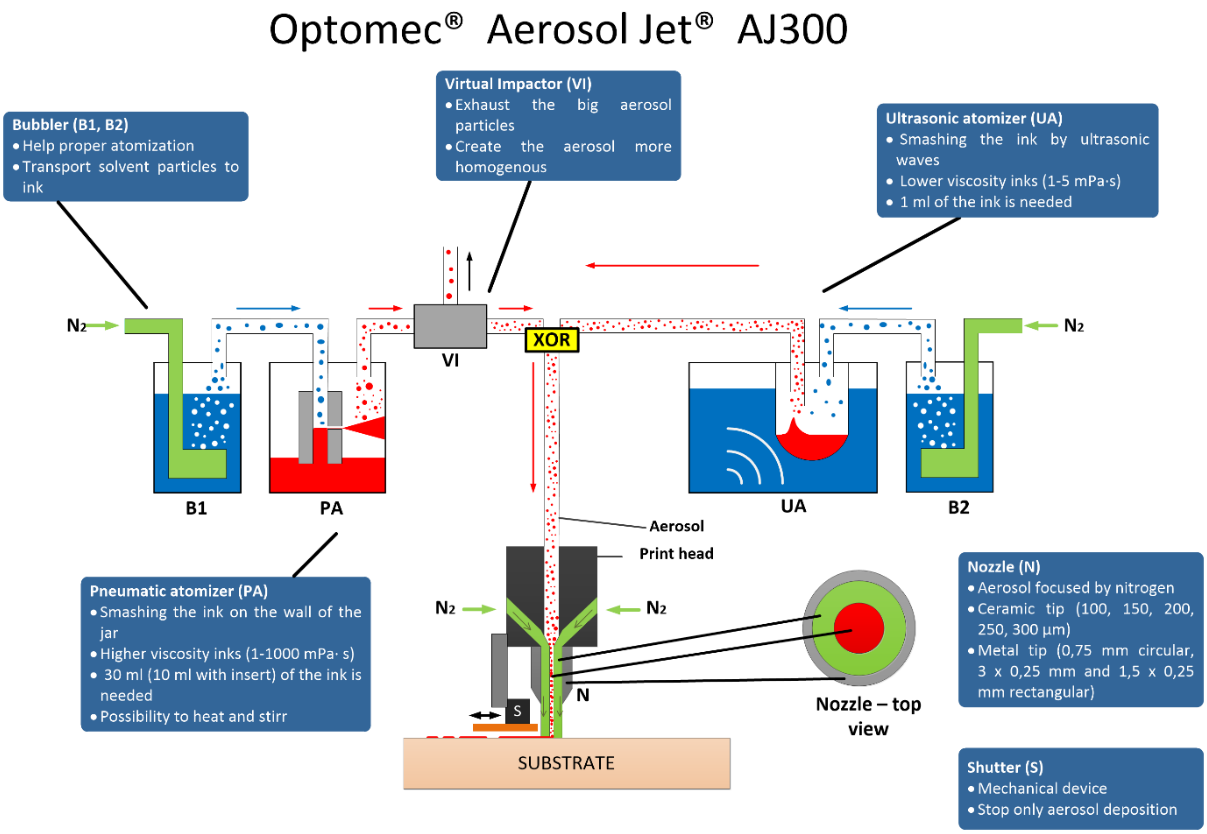

Figure 1: Principle scheme of Aerosol Jet System

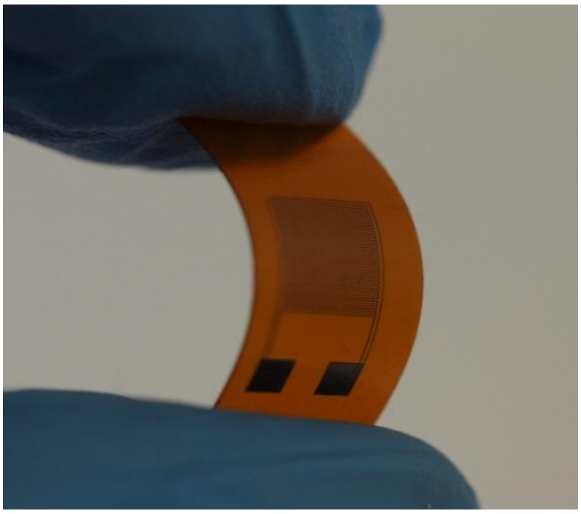

Fig. 2. Printed flexible ammonia sensor

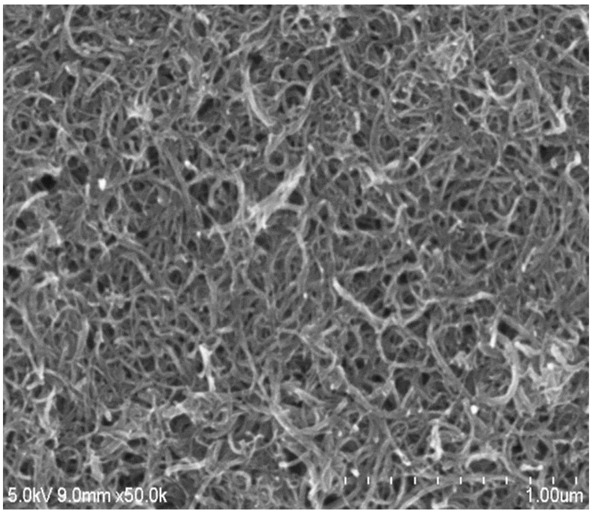

Fig.3. Carbon nanotube net deposited by AJS

Deposited layer underwent the optical inspection by scanning electron microscopy. On the Fig.3 detail of carbon nanotubes net is shown. This figure confirms the assumption that CNT do not create any agglomeration when are printed by aerosol jet system. Results of the experiment shows high sensitivity to ammonia (Fig.4.). For better demonstration axis "x" is recalculate from the resistance to the sensitivity via equation:

$$S = \frac{R_{air} - R_{gas}}{R_{air}} \, x \, 100 \, [\%] \quad (1)$$

Where R_{air} is resistance of the active layer in the normal atmosphere and R_{gas} is resistance of the active layer in gas detection.

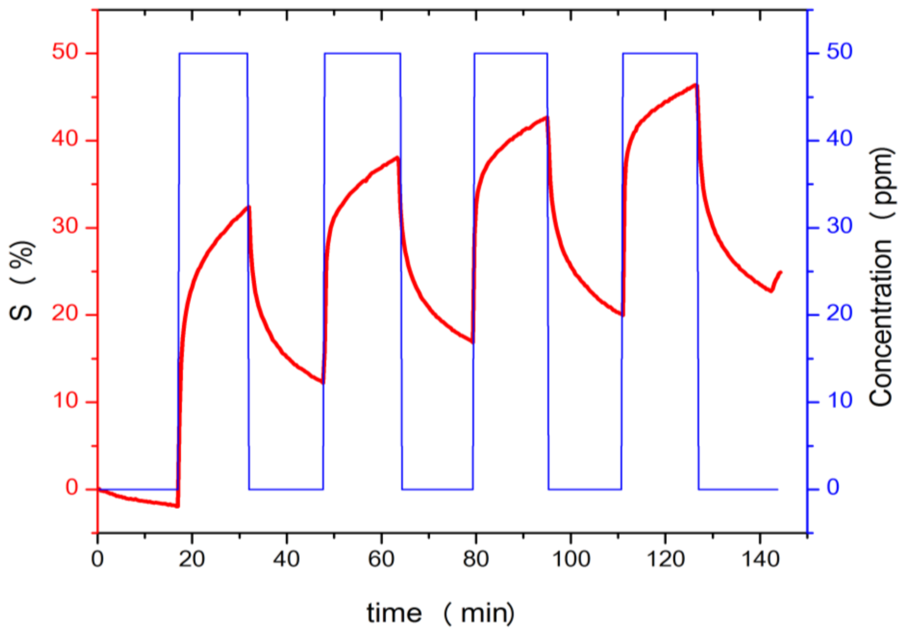

Fig. 4. Sensor response to 50 ppm ammonia

Ammonia detection with raw nanotubes without defects and functional groups is almost impossible. Interaction between the NH_3 molecule and the surface is very weak. Ammonia molecules bind much easier to the site of structural defects on the CNT surface. It can happen only in an inert atmosphere, because under the common atmosphere oxygen is immediately attached to these defects. On the other hand NH_3 molecules bond more easily to oxygen rather than to the CNT wall. The adsorption energy of ammonia is from 12 to 17 kJ · mol $^{-1}$, depending on the rotation of the molecule over the surface of the CNT. Oxygen molecules presence on the surface of the tube bound at the site of the defects (or the ends of the functional groups) leads to increase an adsorption energy to 40 kJ · mol $^{-1}$. According to the theory of chemical bonds and this finding, a hydrogen bond forms between NH3 and O_2 [5]. This can be used advantageously when detecting the gas. As mentioned above, used CNT are non-covalently functionalized by pyrene with SO_3H side groups. Every oxygen ends of the side groups is potential place for the ammonia molecule interaction. This is a reason of the high sensitivity of this CNT type to the ammonia. Moreover, small binding energy of hydrogen bond leads to the partial spontaneous release of NH_3 molecules after removal of the gas. The result of this effect is spontaneous gas desorption from active layer at the room temperature.

Conclusion

The carbon nanotubes was printed by aerosol jet system on flexible substrate. The sensor showed the high sensitivity to ammonia. The resistance increase approximately by 25 % during the gas exposure at the room temperature. CNT deposition by AJS is promising way how to create a thin homogenous layer. This deposition method eliminates the problem of other common deposition techniques where the agglomerates were created during the forming of a layer. Generally, this deposition technique is very suitable for the deposition of all types of carbon nanotubes.

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