

METALLIZATION AND BONDING APPROACH FOR CARBYNE NANOMATERIAL

R. Tomov M. Aleksandrova

*Department of Microelectronics, Technical University of Sofia, Sofia, Bulgaria
rtomov@tu-sofia.bg, m_aleksandrova@tu-sofia.bg*

Abstract- In this paper, carbyne film applicable in gas sensors, was metallized by vacuum sputtering with different materials, aiming formation of Ohmic and Schottky contacts. The metal top layers were bonded by different metal wires and bonding conditions to prepare the samples for packaging. The effect of the bonding force and temperature on the penetration of metal particles in the carbyne was investigated. Silver was bonded by aluminum wire and palladium – by gold wire. The cross-section of the carbyne/metal interface was observed by scanning electron microscope and chemical analysis was made in depth across the layer thickness to explore the elemental profile of each layer. The sheet resistance variation was also used to confirm the results from the interface imaging and mapping. It was found that silver particles diffuse slowly in the carbyne, but the palladium ones diffuse strongly and significantly increase the conductivity of the carbyne material. A possible solution to prevent this process is nickel barrier thin film insertion under the palladium. It was proved that the Pd/Ni interface is stable at bonding and the properties of the carbyne were kept unmodified. The results are of great importance for the prototyping of novel carbon nanomaterials-based gas sensors.

Keywords: Metallization, Bonding, Carbon Nanomaterials, Organic Chips, Carbyne Sensors.

1. INTRODUCTION

The hybridization type of carbon atoms determines the physio-chemical properties of the carbon-based nanomaterials. According to it, three basic forms are known – diamond, graphite and carbyne. Among them, some nanostructures, such as graphite derivatives (carbon nanotubes, graphene and fullerene) are among the most studied for engineering practice [1]. Recently, an allotrope of carbon, called carbyne, having one-dimensional sp-hybridization and linear chain with alternating carbon-carbon single and triple bonds, has attracted the attention of the scientists [2]. Due to its mechanical stability and selectivity to certain chemical compounds, carbyne seems to be very appropriate for fabrication of different sensors for biomedical engineering, environmental monitoring and harmful gases

analyzing [3]. Among the advantages that have been discovered for the carbyne gas sensors, is their ability to respond to small concentrations at room temperature and without light stimulation.

The high temperatures or UV light exposure is usually applied to activate the process of detection at semiconducting metal-oxides or 2D nanomaterials [4, 5]. Carbyne nanocrystals were found to react to nitrogen dioxide gas at concentrations of below 50 ppm at room temperature [6], as well as to ethanol vapors at concentration 70-700 ppm at room temperature [7]. To avoid electrical losses and provide an accurate measurement, the interface conditions between the metal contacts and active (sensitive) layers should be well-defined and controlled. The deposition of metal films plays a crucial role in enhancing the properties of carbyne in several ways. By choosing different metals and controlling the thickness of the metal layer, researchers can manipulate properties such as optical behavior, plasmonic effects, and surface-enhanced Raman spectroscopy (SERS) capability. Metallization of carbyne films with metals like gold and palladium ensures an Ohmic contacts formation. In addition, gold provides the bonding ability property and interconnects. Often, combination of double layers one over another is preferable - the underlayer provides adhesion strength at the metal/organic interface, or serves as an interdiffusion barrier, and the top layer provides the necessary electrical conductivity and bonding ability [8, 9].

While carbyne is known for its incredible mechanical strength, metal films tend to be susceptible to damage. By metallizing carbyne films, a protective metal underlayer can be added, enhancing the mechanical stability and preventing interface degradation under various conditions [10]. Carbyne films typically exhibit poor adhesion to most substrates. Metallization of carbyne films can facilitate strong adhesion between the film and the substrate, improving the overall film quality and durability [11]. Metallizing carbyne films allows for their compatibility and integration with existing electronic devices and fabrication processes. This compatibility opens opportunities for incorporating carbyne films into various technological applications, including biomedical or consumer electronics. The metal films are typically

grown by vacuum deposition process or electrochemistry. However, in the case of nanomaterials, thin film technology, such as vacuum sputtering of single component metal, or vacuum electron-beam evaporation of metal alloys, have been used due to the precise control of the small thicknesses and high purity and uniformity of the resulting films [12].

The aim of this work is to study the bonding ability of multilayer metal systems, forming Ohmic and Schottky contacts with carbyne coatings and to explore how the bonding process with its temperature and pressure affects the mutual interdiffusion of nanoparticles in depth in the underlying materials. The cross-section of the metal-carbyne interface was observed by scanning electron microscope (SEM) to check for delamination or peel-off phenomena of the metal films. Energy dispersive X-ray analysis (EDX) was conducted to determine the elements content of the depth profile of the multilayer stack. The chemical data was gathered in textural context by mapping to observe the variations in chemical composition. The sheet resistance of all films in the stack was measured to follow the electrical conductivity changes if metal particles diffuse into the carbyne and dope it. To the best of the author's knowledge this is the first paper investigating practical problems of carbyne metallization and its quality after the bonding process is applied.

2. MATERIALS AND METHODS

Carbyne-enriched coating was formed on glass substrates, cleaned in standard detergent ammonia-based solution. For the carbyne deposition ion-assisted pulse-plasma sputtering was used. The ion and plasma flows cross over the substrate surface. The ion beam power is responsible for bending in the carbon chains, resulting in stabilization of the formed linear chains. The evaporation of graphite disk is due to localization of e-beam energy, increasing the temperature to 3000 °C. The linear chains of the resulting carbyne are then transferred to the substrate surface to condense. The pulsed plasma energy should exceed the binding energy of the double and triple bonds in the carbyne but should be lower than the binding energy of the sp¹ bonds. The deposition conditions were found to be a target to substrates distance of 1 m; number of carbon plasma pulses equal to 3000; an arc discharge voltage concentrated between the carbon target and the substrate holder of 300 V; capacitor charge forming plasma pulses equal to 2000 µf at 5 Hz; and power of the plasma formed from argon ions, 150 W.

For the metallization of the carbyne, direct-current (DC) sputtering of 3-inches Pd, Ni and Au targets were used for the Ohmic contacts and Al and Ag wire were thermally evaporated for the Schottky contact. Bi-layer systems were designed and were compared before and after bonding. The following combinations were prepared, carbyne/Ag, carbyne/Ag/Al, carbyne/Pd, carbyne/Pd/Au, carbyne/Ni/Pd/Au. Nickel intermediate thin film (15 nm) was used as a barrier to prevent diffusion of Pd nanoparticles into the carbyne. The bonding process was conducted by a semi-automatic ultrasonic wire bonder F&S Bondtec.

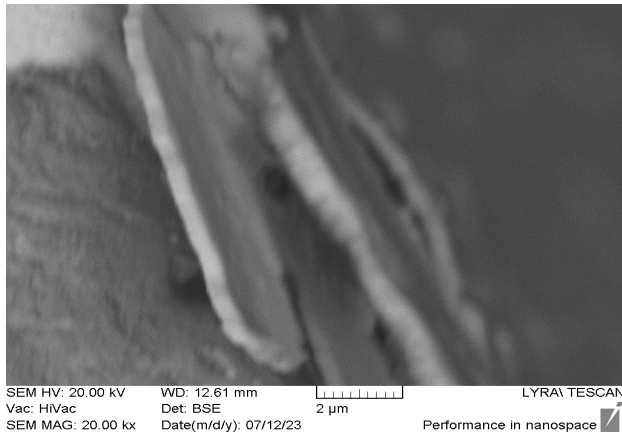
At the standard wire bonding ball-wedge, the second bond is low-strength. For this reason, "stitch-ball" method is used for it, which means preliminary formation of a ball for better stabilization of the bond. It should be also noted that the Pd film is easy bondable by Au wire only and the Ag film is easy bondable by Al wire. The combinations Au film-Au bond and Al film-Al bond are also favorable. The bonding parameters were optimized in term of mechanical strength and were as follows: for the Au bonding wire, bonding temperature 100 °C, bonding force 70 g, ultrasonic power 150 W and bonding time 50 s; for the Al bonding wire, bonding temperature 100 °C, bonding force 50 g, ultrasonic power 120 W and bonding time 30 s.

The sheet resistance measurements were conducted by four-point prober FPP-5000 Veeco. Scanning electron microscopy (SEM) and Energy dispersive X-ray analysis (EDX) were conducted by Lira/Tescan and Bruker AXS Microanalysis GmbH, Germany, respectively.

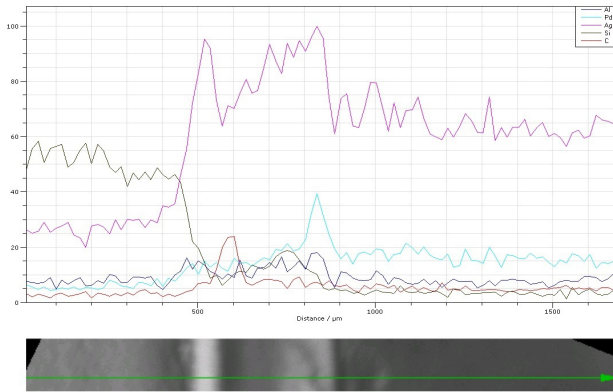
3. RESULTS AND DISCUSSION

Figure 1a shows a SEM image of a cross-sectional view of metallized carbyne with a silver film for a Schottky contact. The layer consists of flake-like silver clusters, forming irregular surfaces. The elemental analysis revealed that silver nanoparticles are not incorporated in the carbyne layer in depth due to the heat generated at deposition. This is evident from the curves corresponding to the distribution of each chemical element. Beyond the Ag film thickness, its corresponding signal attenuated sharply, and the dominant signal comes from the greatest volume of the glass substrate (i.e., the signal of silicon is dominant). Within the silver thickness its signal is the greatest. The sheet resistance of the carbyne measured in 10 points uniformly distributed over an area of 6 cm² was average 0.22 kΩ/sq. The histogram of distribution of the sheet resistance in all positions of the probes is shown in Figure 2a.

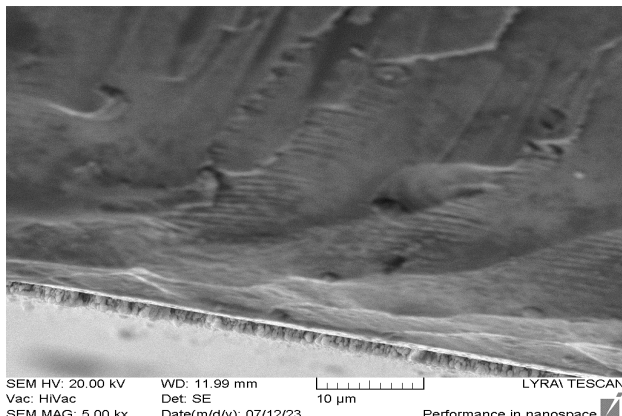
It can be noted a small deviation from the average values, although the flake-like structure of the metallization layer. This is an indication of a very good planarity and uniformity of the Ag coated carbyne material. After application of the bonding tool, and the bonding process finalize, a modification of the silver layer occurred. This is shown in Figure 1b, where it is seen (at the bottom side) columnar-granular transformation, resulting in local irregularities of the silver film. This is visible from the drops of the signal associated to this metal from the EDX analysis. Nevertheless, the silver didn't peel-off and resisted at pull-off load of 50 g. There is negligible reduction of the carbyne's sheet resistance to 0.20 kΩ/sq, or approximately 12% difference with the non-bonded system carbyne/Ag. The change of the film's conductivity can be ascribed to surface poor enriching with silver nanoparticles because of the joint effect of temperature and pressure from the bonding tool, resulting in a small portion of Ag particles diffusing. Due to slow diffusion rate of the atoms [13]. As can be seen from Figure 2b, the bonding process deteriorates the uniformity of the film, according to the histogram bars.



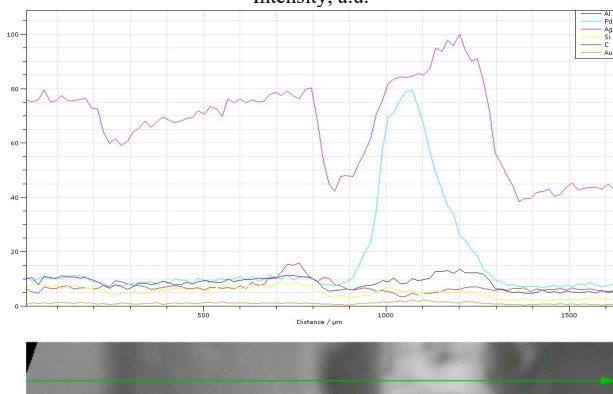
Intensity, a.u.



(a)

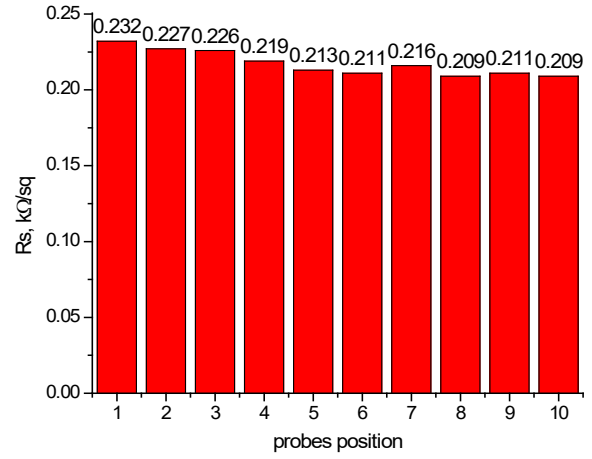


Intensity, a.u.

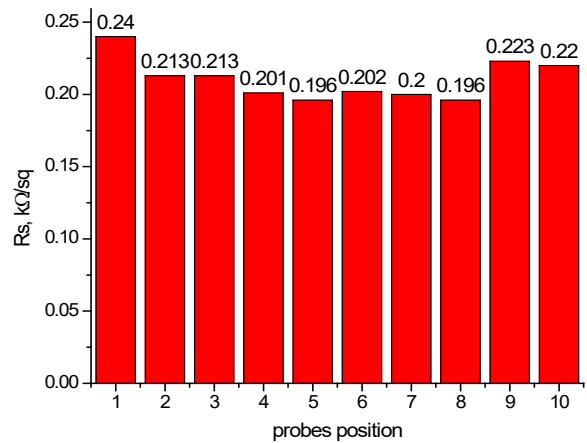


(b)

Figure 1. SEM image of the cross-sectional view and elemental analysis in the cut for: a. carbyne/Ag (top); b. carbyne/Ag/Al bond (top)



(a)



(b)

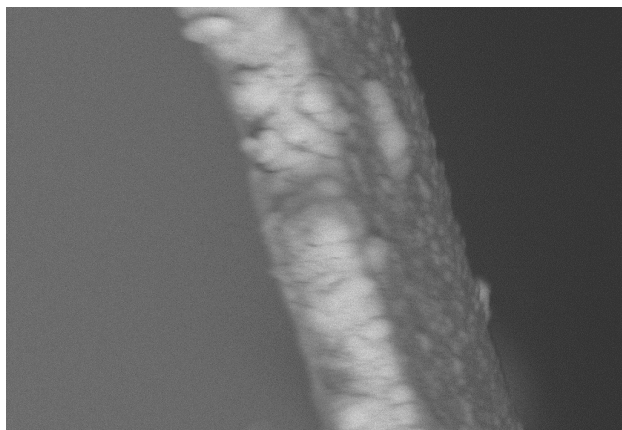
Figure 2. Sheet resistance of the carbyne for the cases a) carbyne/Ag and b) carbyne/Ag/Al bond

Figure 3a shows a SEM image of a cross-sectional view of metallized carbyne with a palladium film for an Ohmic contact. The layer consists of granular particles, forming multiple grain interfaces with similar size, organized in a uniform, flat surface. The average sheet resistance of the Pd/carbyne bi-layer system before bonding was ~ 0.87 k Ω /sq with small deviation across the sample area, as is visible from the flat histogram, shown in Figure 4a. The elemental analysis revealed that Pd nanoparticles tend to incorporate in the carbyne layer in depth due to the heat generated at deposition.

According to the EDX, at a probing depth beyond the Pd film thickness, the corresponding signal indicating its concentration attenuates less than twice. This process is accelerated with the supplied bonding temperature and pressure, as is visible from the sheet resistance measurements (Figure 4b), indicating drop of the sheet resistance to average 0.49 k Ω /sq, which is almost twice decrease, as compared to the case before Pd metallization bonding. Similarly, as in the case of silver bonding, the deviation from the average value of the sheet resistance is deteriorated because of the bonding process, which confirms the results from EDX for doping of carbyne with palladium.

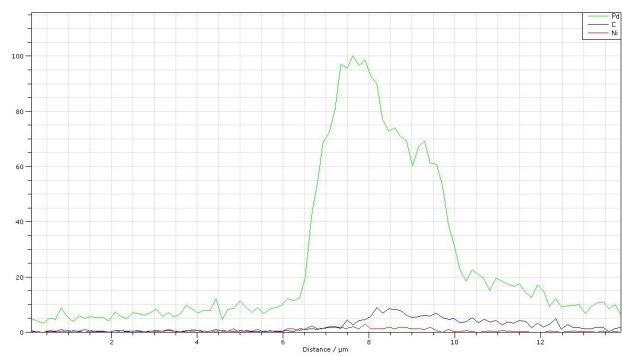
To prevent this phenomenon, a barrier thin film of nickel with a thickness of ~ 15 nm was inserted as intermediate (or diffusion blocking) layer. As a first result, the grown Pd film has no large sized granular structure (Figure 3b), making the surface flatter and more favorable for high-quality bonding with uniform distribution of the pressure and heat during the micro welding process. Secondly, the Ni was found to be a very efficient diffusion barrier, as the sheet resistance of the carbyne included in the bi-layer metallization system of Ni/Pd was measured to be ~ 0.94 k Ω /sq that is close to the carbyne single layer (Figure 4c).

The bonding process results in a fine columnar growth of the Pd over the Ni, without granular microstructure. In addition, there is a sharp discontinuing of the Pd corresponding line in the elemental analysis beyond the Pd film thickness (Figure 3c). The Ni signal within the thickness of palladium is negligible and can be ascribed to contaminating particles incorporated due to the deposition of the two materials consequently in a common vacuum cycle of sputtering. The variation of the sheet resistance after bonding is ~ 0.85 k Ω /sq, which is less than 10% (Figure 4d) and confirms the results from the EDX suggesting that the carbyne is not doped by Pd in case of Ni underlayer. Therefore, the Ni materials can be considered as an efficient barrier blocking the diffusion of palladium.

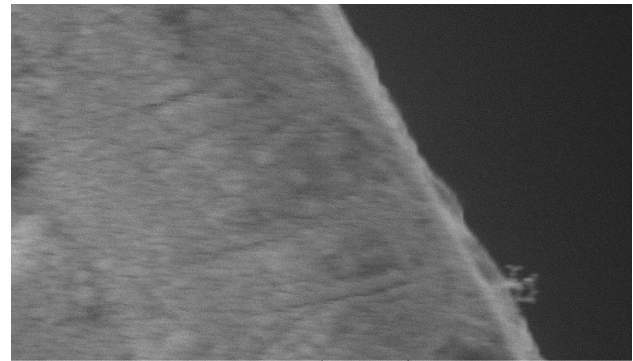


SEM HV: 20.00 kV WD: 10.68 mm
Vac: HiVac Det: BSE
SEM MAG: 20.01 kx Date(m/d/y): 07/19/23

Intensity, a.u.

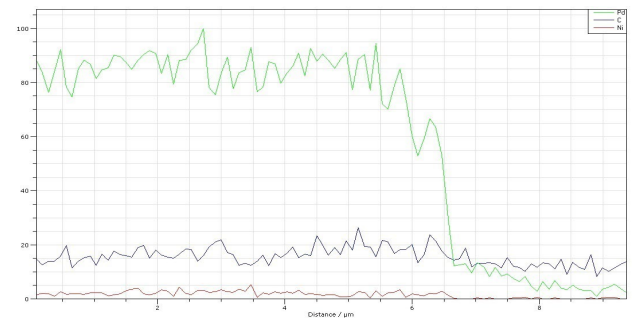


(a)

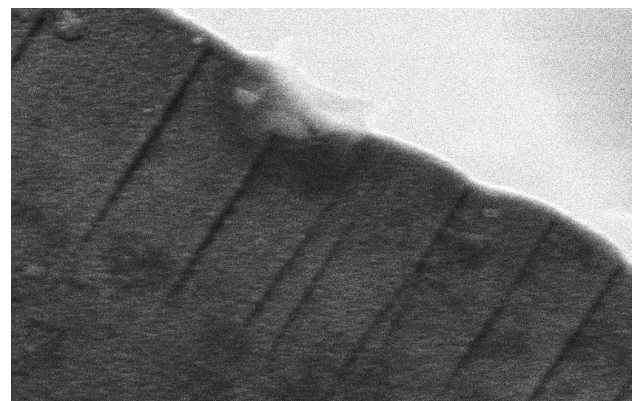


SEM HV: 20.00 kV WD: 12.38 mm
Vac: HiVac Det: SE
SEM MAG: 20.00 kx Date(m/d/y): 07/19/23

Intensity, a.u.

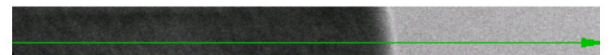
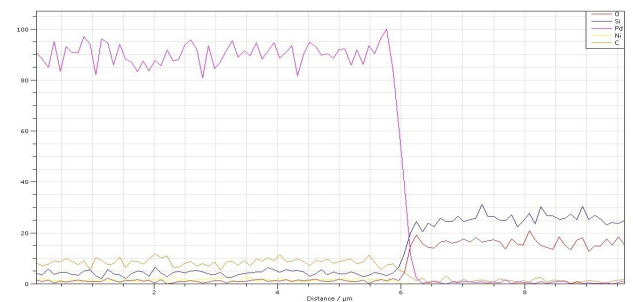


(b)



SEM HV: 20.00 kV WD: 11.28 mm
Vac: HiVac Det: SE
SEM MAG: 16.44 kx Date(m/d/y): 07/19/23

Intensity, a.u.



(c)

Figure 3. SEM image of the cross-sectional view and elemental analysis in the cut for: a. carbyne/Pd (top), b. carbyne/Ni/Pd (top), c. carbyne/Ni/Pd/Au bond (top)

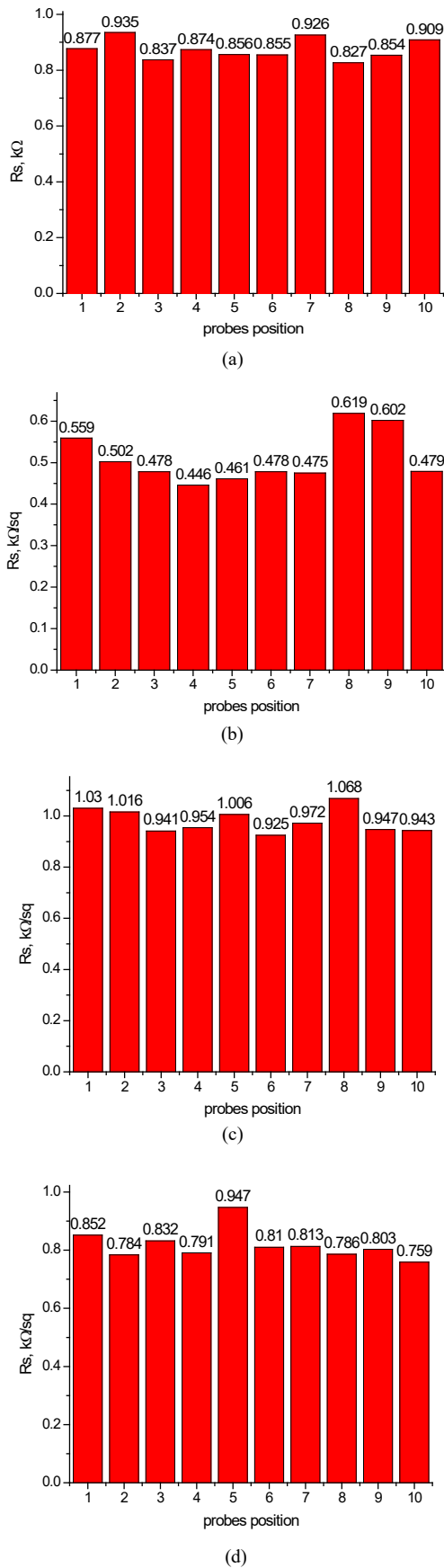


Figure 4. Sheet resistance of: a. Pd/carbyne before bonding, b. Pd/carbyne after bonding, c. Pd/Ni/carbyne before bonding, d. Pd/Ni/carbyne after bonding

The limitation of the present study is the bonding temperature, which is expected to result in a lower contact resistance at the interface of carbyne with the metal contacts and to promote the mechanical strength of the bond due to improved adhesion. However, this may cause an acceleration of the particle's diffusion even through the nickel barrier layers. This layer cannot be grown with a higher thickness, because the Ohmic characteristics of the contact will be modified. A possible avenue for further research to improve the metallization process and enhance film properties can be metal alloy composition. Conducting research on silver-palladium alloy compositions can offer insights into improving film properties. Exploring different ratios of silver and palladium in the metal film can help optimize conductivity, adhesion, corrosion resistance, and other desirable properties. It can also be interesting to investigate the effect of introducing other types of metals or metal nanoparticles into the alloy composition.

4. CONCLUSION

The combinations of silver and palladium films on carbyne have not been extensively explored in the literature. This is the first report on the microstructural properties, chemical analysis and electrical conductance measurement of the interfaces Pd/carbyne and Ag/carbyne. The bonding conditions affect the quality of this interface and accelerate the diffusion of particles for the case of Pd film. This problem can be overcome with a nickel barrier film, which prevents the deterioration of the interface and stabilizes the sheet resistance of the carbyne even after bonding procedure. In summary, metallization of carbyne films is significant for their connectivity to packaging for the needs of the electronic devices. Metal films can also promote adhesion, enabling tunable properties, and facilitating integration of new carbon-based nanomaterials with existing technologies. These advancements broaden the potential applications of carbyne films in various fields, ranging from electronics and sensing to energy storage and beyond.

Future direction of research might be doping of carbyne with metal particles and investigate this phenomenon as a useful tool for realization of carbyne-metal nanocomposite with tuning properties. Investigating the structural changes and interactions that occur when metal films are deposited on carbyne could provide insights into the structural stability, strain distribution, and electronic properties of metal-carbyne composites. The interface between metal films and carbyne is expected to play a vital role in determining the overall performance of these hybrid systems. Investigating the interfacial properties, charge transfer mechanisms, and the influence of different metal species could provide insights into optimizing the interaction and improving the overall performance of metal-carbyne composites and the metal/carbyne interfaces.

ACKNOWLEDGEMENTS

This work is funded by the National program "Young Scientists and Postdoctoral Researchers, 2" of the Ministry of Education and Science, Bulgaria. The authors are thankful to Assist. Prof. Atanas Tzonev from Sofia University, Sofia, Bulgaria for the SEM/EDX analysis and Dr. Georgi Kolev for the assistance at bonding.

REFERENCES

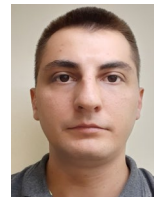
- [1] S.X.L. Luo, T.M. Swager, "Chemoreceptive Sensing with Functionalized Carbon Nanotubes", *Nat. Rev. Meth. Primers*, Vol. 3, No. 73, pp. 1-23, 2023.
- [2] G. Yang, "Synthesis, Properties, and Applications of Carbyne Nanocrystals", *Mat. Sci. Eng.: R: Reports*, Vol. 151, No. 100692, pp. 1-52, 2022.
- [3] M. Aleksandrova, G. Kolev, G. Dobrikov, A. Brigadin, A. Lukin, "Unlocking the Carbyne-Enriched Nanocoating Sensitivity to Volatile Organic Vapors with Plasma-Driven Deposition onto Bulk Micromachined Silicon Membranes", *Nanomaterials*, Vol. 12, No. 2066, pp. 1-11, 2022.
- [4] J. Yu, Z.A. Tang, G.Z. Yan, P.C.H. Chan, Z.X. Huang, "An Experimental Study on Micro-Gas Sensors with Strip Shape Tin Oxide Thin Films", *Sens. Actuators B Chem.*, Vol. 139, No. 2, pp. 346-350, 2009.
- [5] E. Lee, Y.S. Yoon, D. Kim, "Two-Dimensional Transition Metal Dichalcogenides and Metal Oxide Hybrids for Gas Sensing", *ACS Sens.*, Vol. 3, No. 10, pp. 2045-2060, 2018.
- [6] F. Yang, Z. Zheng, Z. Lin, B. Wang, P. Liu, G. Yang, "Visible-Light-Driven Room-Temperature Gas Sensor Based on Carbyne Nanocrystals", *Sens. Actuators B: Chem.*, Vol. 316, No. 128200, pp. 1-9, 2020.
- [7] M. Aleksandrova, G. Kolev, A. Brigadin, A. Lukin, "Gas-Sensing Properties of a Carbyne-Enriched Nanocoating Deposited onto Surface Acoustic Wave Composite Substrates with Various Electrode Topologies", *Crystals*, Vol. 12, No. 4, Art. No. 501, pp. 1-12, 2022.
- [8] K. Son, et al., "Effects of NCF and UBM Materials on Electromigration Reliabilities of Sn-Ag Micropumps for Advanced 3D Packaging", *The 69th Electronic Components and Technology Conference (ECTC)*, pp. 2246-2251, Las Vegas, NV, USA, 28-31 May 2019.
- [9] A.M. Hashimov, K.Sh. Gahramanov, I.T. Mamedova, M.A. Hasanov, S.Sh. Gahramanov, N.M. Abdullayev, "Technology of Obtaining Thin Films from a Foil $A^V_2B^{VI}_3$ ", *International Journal on Technical and Physical Problems of Engineering (IJTPE)*, Issue 32, Vol. 9, No. 3, pp. 35-38, September 2017.
- [10] K. Wu, J.Y. Zhang, P. Zhang, Y.Q. Wang, G. Liun, G.J. Zhang, J. Sun, "Fracture Behavior and Adhesion Energy of Nanostructured Cu/Mo Multilayer Films", *Mat. Sci. Eng.: A*, Vol. 613, pp. 130-135, 2014.

[11] A.A. Hamid, H.A.M. Al Jewaree, "A Practical Measurements of Friction Coefficients During Compaction Process of Different Ceramic Powders", *International Journal on Technical and Physical Problems of Engineering (IJTPE)*, Issue 54, Vol. 15, No. 1, pp. 283-287, March 2023.

[12] Y. Lian, "Semiconductor Microchips and Fabrication, A Practical Guide to Theory and Manufacturing", Wiley-IEEE Press, pp. 271-291, New Jersey, USA, 2022.

[13] T. Gietzelt, M. Walter, V. Toth, F. Messerschmidt, M. Blem, "Comprehensive Study of the Influence of the Bonding Temperature and Contact Pressure Regimes During Diffusion Bonding on the Deformation and Mechanical Properties of AISI 304", *Adv. Eng. Mater.*, Vol. 23, No. 2100188, pp. 1-15, 2021.

BIOGRAPHIES



Name: Rade

Surname: Tomov

Birthdate: 06.11.1995

Birthplace: Dimitrovgrad, Serbia

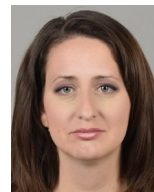
Bachelor: Engineering in Micro-Electronics, Technical University of Sofia, Sofia, Bulgaria, 2020

Master: Engineering, Microtechnology and Nanoengineering, Technical University of Sofia, Sofia, Bulgaria, 2021

Doctorate: Student, Researcher, Technology of Electronic Fabrication, Technical University of Sofia, Sofia, Bulgaria, Since 2022

Research Interests: Organic Nanomaterials, Metallization Systems

Scientific Publications: 5 Papers, 3 Projects



Name: Mariya

Surname: Aleksandrova

Birthdate: 07.01.1983

Birthplace: Sofia, Bulgaria

Bachelor: Engineering, Micro-Electronics, Technical University of Sofia, Sofia, Bulgaria, 2005

Master: Engineering, Microelectronics, Technical University of Sofia, Sofia, Bulgaria, 2007

Doctorate: Technology of Electronic Fabrication, Technical University of Sofia, Sofia, Bulgaria, 2010

The Last Scientific Position: Assoc. Prof., Department of Microelectronics, Technical University of Sofia, Sofia Bulgaria, Since 2015

Research Interests: Organic Electronics, Flexible Electronics, Thin-Film Electronics

Scientific Publications: 120 Papers, 15 Projects

Scientific Membership: Bulgarian Union of Scientists, 2018