



Article Physicochemical Fundamentals of the Synthesis of a Cu@BN Composite Consisting of Nanosized Copper Enclosed in a Boron Nitride Matrix

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Abstract: The thermal reduction of the copper(II) complexes $[Cu^{II}(N_2H_4)_3][B_{10}H_{10}] \cdot nH_2O$ (I·nH₂O) and $[Cu^{II}(NH_3)_4][B_{10}H_{10}] \cdot nH_2O$ (II·nH₂O) has been studied in an argon atmosphere at 900 °C. It has been found that the annealing of both compounds results in a Cu@BN boron-containing copper composite. It has been shown that this process leads to the formation of a boron nitride matrix doped with cubic copper(0) nanoparticles due to the copper(II) \rightarrow copper(I) \rightarrow copper(0) thermal reduction. The phase composition of annealing products I⁹⁰⁰ and II⁹⁰⁰ has been determined based on powder X-ray diffraction, IR spectroscopy and thermal analysis data. The morphology, average particle size and composition of the composite have been determined by TEM and high-resolution TEM + EDS. The average particle size has been found to be about 81 nm and 52 nm for samples I⁹⁰⁰ and II⁹⁰⁰, respectively. Comparison of the results obtained using physicochemical studies has shown the identity of the composition of the products of annealing I⁹⁰⁰ and II⁹⁰⁰. The electrical properties of a coating based on an I⁹⁰⁰ sample modified with Cu⁰ \rightarrow Cu₂O in situ during deposition on a chip at 300 °C in air have been studied. As a result, with increasing temperature, an increase in the electrical conductivity characteristic of semiconductors has been observed.

Keywords: copper; nanoparticles; thermal reduction; conductivity; decahydro-closo-decaborate anion

1. Introduction

To date, the vast majority of publications devoted to boron cluster anions are associated with their use in medicine [1–7]. Nevertheless, these compounds are promising objects for research in materials science, in particular, for the preparation of hypergolic fuels [8–11], luminescent materials [12–16] or binary boron-containing materials with different properties [17–24]. We have previously shown that the thermolysis of cobalt coordination compounds with boron cluster anions as counterions $[Co(DMF)_6][An]$, where An = $[B_{12}H_{12}]^{2-}$, $[trans-B_{20}H_{18}]^{2-}$ or $[B_{10}Cl_{10}]^{2-}$, at 900 °C in an argon atmosphere made it possible to obtain nanocrystalline cobalt boride in one stage [24]. In this case, variation in the nature of the boron cluster anions used can affect both the phase composition (the formation of a boride on a boron nitride matrix or in the form of an individual compound) and the structural features of the formed cobalt monoboride. In the case of thermolysis of nickel(II) and cobalt(II) complexes with the *closo*-decaborate anion $[M(solv)_6][B_{10}H_{10}]$ (M = Co, Ni; solv = H₂O, N₂H₄, DMF, DMSO) [25–27], two-component systems have been obtained: a boron-containing phase and binary metal compounds. In particular, the thermolysis of the nickel(II) complex [Ni(DMF)_6][B_{10}H_{10}] led to the formation of



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). the solid solution $Ni_3C_{1-x}B_x + Ni_3C$ [26], while the thermolysis of the cobalt(II) complex $[Co(N_2H_4)_3][B_{10}H_{10}]$ led to the BN boron nitride phase and dicobalt boride Co_2B [27].

The preparation of copper compounds is an urgent task. The remarkable properties of these compounds [28–35] determine their wide application as thermoelectric materials [36–38], materials for solar batteries [39–41], and photocatalysts [42,43].

Here, the thermal reduction of amine- and hydrazine-containing copper(II) coordination compounds $[Cu^{II}(N_2H_4)_3][B_{10}H_{10}]\cdot nH_2O$ (I· nH_2O) and $[Cu^{II}(NH_3)_4][B_{10}H_{10}]\cdot nH_2O$ (II· nH_2O) have been studied, and the electrical properties of a coating prepared based on thermolysis products have been measured.

2. Experimental

2.1. Synthesis of Compounds

All the reactions were performed in air. Commercially available hydrazine hydrate (N₂H₄·H₂O, 80% aqueous solution) and ammonium hydroxide solution (NH₄OH, 28.0–30.0% NH₃ basis) were purchased from Merck KGaA, Darmstadt, Germany and used without additional purification. $\{Cu_2[B_{10}H_{10}]\}_n$ was synthesized according to the procedure reported [44].

2.1.1. $[Cu^{II}(N_2H_4)_3][B_{10}H_{10}] \cdot nH_2O (I \cdot nH_2O)$ and $[Cu^{II}(NH_3)_4][B_{10}H_{10}] \cdot nH_2O (II \cdot nH_2O)$

Coordination compounds $I \cdot nH_2O$ and $II \cdot nH_2O$ were obtained by recrystallization of copper(I) complex $\{Cu_2[B_{10}H_{10}]\}_n$ (15 mmol) from a solution of $N_2H_4 \cdot H_2O$ (10 mL) or NH_4OH (10 mL), respectively. After evaporation in air for 48 h, polycrystalline precipitates of dark blue ($I \cdot nH_2O$) or blue ($II \cdot nH_2O$) color were isolated from the reaction solutions. The precipitates were filtered off and dried in air. The yield with respect to boron was ~60% for $I \cdot nH_2O$ and ~64% for $II \cdot nH_2O$.

I: Calcd. for CuH₂₂N₆B₁₀, %: H, 7.98; N, 30.24; Cu, 22.87; B, 38.9. Found, %: H, 8.05; N, 30.18; Cu, 22.93; B, 38.2. IR (NaCl, Nujol, cm⁻¹): ν (OH) 3500–3300; ν (NH) 3297, 3239; ν (BH) 2461, 2412, 2339.

II: Calcd. for CuH₂₂N₄B₁₀, %: H, 8.87; N, 22.42; Cu, 25.43; B, 43.3. Found, %: H, 8.94; N, 22.47; Cu, 25.49; B, 42.9. IR (NaCl, Nujol, cm⁻¹): ν (OH) 3550–3400; ν (NH) ~3191; ν (BH) 2498, 2467, 2449.

2.1.2. Samples I^{900} and II^{900}

Black powders of samples I^{900} and II^{900} were obtained by the annealing of compounds $I \cdot nH_2O$ and $II \cdot nH_2O$ in a quartz tube-reactor heated by a resistance furnace and sealed with a ground joint. The studied samples were placed in corundum crucibles. Annealing was carried out in an argon flow at a gas flow rate of 300 mL/min and heating at 10 °C/min. The samples were kept at a given temperature for 120 min.

2.2. Methods of Investigation

Elemental analysis for carbon, hydrogen, and nitrogen was performed using a Carlo ErbaCHNS-3 FA 1108 (Milan, Italy) automated elemental analyzer. Boron and metal content was determined on an iCAP 6300 Duo ICP emission spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) with inductively coupled plasma.

IR spectra of compounds were recorded on a Infralum FT-02 Fourier-transform spectrophotometer (Lumex, Saint Petersburg, Russia) in the range of 4000–600 cm⁻¹ at a resolution of 1 cm⁻¹. Samples were prepared as Nujol mulls; NaCl pellets were used for measurements.

X-ray powder diffraction studies were performed on a Bruker D8 ADVANCE diffractometer (BRUKER AXS GmbH, Karlsruhe, Germany) (CuK_{α} radiation, Ni filter, LYNXEYE detector, reflection geometry) in low-background cuvettes with an oriented silicon single crystal substrate in the angle range $2\theta = 5-80^{\circ}$ with a step 0.01125° (Figure S1).

Thermogravimetric analysis of $I \cdot nH_2O$ and $II \cdot nH_2O$ samples was performed by DSC-TGA using an SDT Q600 thermal analyzer (TA Instruments, New Castle, DE, USA) in alundum crucibles with a volume of 90 μ L in high-purity argon flow (flow rate 100 mL per minute); the temperature range was RT-800 °C, and the sample heating rate was 10 °C/min.

Samples $I \cdot nH_2O$ and $II \cdot nH_2O$ were annealed in a Nabertherm R 30/200/11 tube furnace (Nabertherm GmbH, Lilienthal, Germany) in an inert gas flow. Before annealing, samples were ground in an agate mortar and transferred into thin-walled quartz test tubes, which were then placed in a quartz flow tube at the level of the furnace hot zone.

Transmission electron microscopy (TEM) studies of samples I⁹⁰⁰ and II⁹⁰⁰ were carried out on a Jem-1001 instrument (JEOL, Tokyo, Japan) with an accelerating voltage of 80 kV. The morphology of inorganic materials was analyzed using high-resolution TEM on a JEOL JEM-2100 (JEOL, Tokyo, Japan) F/Cs/GIF/EDS device attached to an EDS analyzer.

The material was deposited on copper grids by spraying a suspension in ultrasound.

The particle size distribution was built by measuring the particle sizes visible in the micrograph. The measurement step δ was chosen so that the maximum particle size was about 10 δ . Then the number of particles was counted, the size of which fit into each of the ranges $0-\delta$, $1\delta-2\delta$, etc. The average particle size was calculated using the formula:

$$d_{cp} = \sum_{i} n_1 \cdot \delta\left(i - \frac{1}{2}\right),\tag{1}$$

where n_1 is the number of particles with size from $(i - 1)\delta$ to $i\delta$.

The electrical conductivity of sample I^{900} was studied on a specialized Pt/Al₂O₃/Pt chip using functional ink, which is a dispersed system suitable for microplotter printing of the corresponding coating.

3. Results and Discussion

Precursor complexes containing easily removed ligands have shown their efficiency in the synthesis of metal borides and related compounds [24–27]. In the present study, copper(II) complexes with hydrazine (N_2H_4) and ammonia (NH_3) were chosen as precursor complexes.

3.1. Synthesis of Precursor Compounds $[Cu^{II}(N_2H_4)_3][B_{10}H_{10}] \cdot nH_2O$ (**I** $\cdot nH_2O$) and $[Cu^{II}(NH_3)_4][B_{10}H_{10}] \cdot nH_2O$ (**II** $\cdot nH_2O$)

Mononuclear copper(II) coordination compounds with hydrazine $[Cu^{II}(N_2H_4)_3][B_{10}H_{10}] \cdot nH_2O$ (I· nH_2O) and ammonia $[Cu^{II}(NH_3)_4][B_{10}H_{10}] \cdot nH_2O$ (II· nH_2O) were obtained in the course of a redox reaction when recrystallizing $\{Cu^{I_2}[B_{10}H_{10}]\}_n$ from a solution of hydrazine hydrate (N₂H₄·H₂O) or an aqueous solution of ammonia (NH₄OH) in air (Scheme 1).



Scheme 1. Synthesis of compounds $[Cu^{II}(N_2H_4)_3][B_{10}H_{10}] \cdot nH_2O (I \cdot nH_2O)$ and $[Cu^{II}(NH_3)_4][B_{10}H_{10}] \cdot nH_2O (II \cdot nH_2O)$.

3.2. TGA and IR Data Obtained for Compounds I·nH₂O and II·nH₂O

The obtained compounds were identified and characterized by a set of physicochemical methods of analysis. In the IR spectra of the synthesized compounds $I \cdot nH_2O$ and $II \cdot nH_2O$, there is an intense band of stretching vibrations of BH bonds v(BH) in the range



of 2500–2300 cm⁻¹, which is characteristic of the $[B_{10}H_{10}]^{2-}$ anion acting as a counterion (Figure 1).

Figure 1. IR spectra of starting complex $\{Cu_2[B_{10}H_{10}]\}_n$ (blue) and compounds $I \cdot nH_2O$ (purple) and $II \cdot nH_2O$ (red).

The coordination of NH₃ and N₂H₄ molecules by the metal atom is evidenced by the appearance of stretching vibration bands ν (NH) at 3297 and 3229 cm⁻¹ in the IR spectrum of complex [Cu^{II}(N₂H₄)₃][B₁₀H₁₀]·*n*H₂O (I·*n*H₂O) and ~3191 cm⁻¹ in the IR spectrum of compound [Cu^{II}(NH₃)₄][B₁₀H₁₀]·*n*H₂O (II·*n*H₂O). The presence of a broadened absorption band of ν (OH)_{H2O} stretching vibrations in the region of 3550–3300 cm⁻¹ indicates the presence of solvated water molecules in compounds I·*n*H₂O and II·*n*H₂O.

To determine the annealing regime for precursor complexes, they were initially analyzed by thermogravimetric analysis in argon. For the convenience of identifying the annealing products, the following designations have been introduced: \mathbf{I}^t , \mathbf{II}^t (*t* is temperature).

On the thermogram of complex $I \cdot nH_2O$, three pronounced thermal effects are observed (Figure 2). To correctly assign the data from thermogravimetric analysis, sample $I \cdot nH_2O$ was additionally annealed step by step under the same conditions at temperatures of 135 and 220 °C.

- (1) A broad endothermic effect with a maximum at 130 °C accompanied by a sample weight loss of 5.47% corresponds to the partial removal of solvated water molecules. This is also evidenced by the data from the IR spectrum of sample I^{135} , in which there is a decrease in the intensity of the broadened band of stretching vibrations $\nu(OH)_{H2O}$ at about 3400 cm⁻¹ and the band of bending vibrations $\delta(HOH)$ at 1620 cm⁻¹, observed in the spectrum of sample I (Figure 3).
- (2) The exothermic effect with a maximum at 213 °C corresponds to the exothermic decomposition of hydrazine molecules in the sample and its complete hydration, while the weight loss of the sample is 4.23%. The decomposition of hydrazine molecules is evidenced by the data from the IR spectrum of sample I^{220} , in which there are no $\nu(NH)_{N2H4}$ stretching vibration bands. In addition, when the sample is heated to 220 °C, in the presence of hydrazine molecules exhibiting reducing properties, the reduction of Cu(II) to Cu(I) and the formation of a Cu(I) complex with the $[B_{10}H_{10}]^{2-1}$

anion as a ligand is observed. Thus, in the IR spectrum of sample I^{220} , along with the bands of stretching vibrations of free BH bonds $\nu(BH)$, a new broadened band appears in the range of 2300–2150 cm⁻¹, which is characteristic of stretching vibrations of the BH groups involved in the three-center CuHB bonds, $\nu(BH)_{CuHB}$ (Figure 3). Note that the pattern of the IR spectrum of sample I^{220} in the region of $\nu(BH)$ is similar to the spectrum of complex $\{Cu_2[B_{10}H_{10}]\}_n$ (Figure 1).



Figure 2. Thermogram of compound $I \cdot nH_2O$.



Figure 3. IR spectra of compounds I·*n*H₂O (blue), I¹³⁵ (purple) and I²²⁰ (red).

Thus, taking into account the total mass loss of the sample equal to 11.19%, it can be concluded that in the temperature range of 20–300 °C, the removal of water and ammonia molecules is observed; the latter are formed during the thermal decomposition of the hydrazine molecule, and the total mass loss of the latter is 11.84%.

(3) The heating of sample I·*n*H₂O above 300 °C leads to the destruction of the *closo*-decaborate anion and is accompanied by an exothermic effect with a maximum at 323 °C. At this stage, apparently, the processes associated with the reduction of Cu(I)→Cu(0) come to an end. This assumption is not contradicted by the change in the TG curve and the absence of pronounced thermal effects, which may be associated with the oxidation of Cu(0) by trace amounts of oxygen in the gas used.

On the thermogram of sample $II \cdot nH_2O$, two pronounced thermal effects are observed (Figure 4). An endothermic effect with a maximum at 150 °C and an exothermic one at 384 °C accompanied by a loss of sample weight on the TG curve of 25.45% are observed. The endothermic effect corresponds to the removal of a water molecule and two ammonia molecules, which corresponds to a theoretical mass loss of 25.79%. It should be noted that the shape of the TG curve above 400 °C is similar to the shape of the TG curve of sample $I \cdot nH_2O$ at the same temperatures and, apparently, is due to the processes described above.



Figure 4. Thermogram of compound $II \cdot nH_2O$.

Based on the results of thermogravimetric analysis, the temperature range of sample annealing was determined to be 900 $^{\circ}$ C.

3.3. Thermal Reduction of Compounds I·nH₂O and II·nH₂O

The completion of pyrolysis of compounds $I \cdot nH_2O$ and $II \cdot nH_2O$, as well as the phase composition of samples I^{900} and II^{900} , were determined based on X-ray powder diffraction and IR spectroscopy data.

According to X-ray powder diffraction data, the annealing products I^{900} and II^{900} are two-phase mixtures (Figure 5 and Figure S1). The diffraction patterns of the annealed samples contain reflections corresponding to both boron nitride (BN) and metallic copper, both with cubic modifications; due to the close parameters of unit cells, reflections from these phases merge.



Figure 5. X-ray powder diffraction pattern for sample I⁹⁰⁰.

The IR spectroscopy data do not contradict the X-ray powder diffraction data. Thus, the absence of absorption bands of stretching vibrations v(BH) in the range of 2500–2100 cm⁻¹ in the IR spectra of samples I^{900} and II^{900} , as well as bands of stretching vibrations v(NH) of organic ligands or organic cations in the range 3300–3100 cm⁻¹, indicates complete destruction of the boron cluster anions and organic molecules (Figure 6). The presence of an absorption band at ~790 cm⁻¹, which, according to the literature data [45], refers to stretching vibrations of the v(BN) bond, indicates the formation of a boron nitride phase in the annealed samples. In addition, the presence of absorption bands at ~1100 and ~798 cm⁻¹, as well as the correlation with the IR spectrum of amorphous boron, suggests the presence of an amorphous boron phase in the annealed samples.



Figure 6. IR spectra of samples I⁹⁰⁰ (blue), II⁹⁰⁰ (purple) and amorphous boron (red).

It should be noted that based on the TGA, X-ray powder diffraction, and IR data, the composition and structure of products I^{900} and II^{900} are the same and correspond to the general formula Cu-2BN-8B_{am}.

3.4. Morphology of Samples I⁹⁰⁰ and II⁹⁰⁰

According to the transmission electron microscopy (TEM) data, sample I^{900} is a multicomponent system consisting of individual disparate crystallites formed by the boron nitride phase and amorphous boron agglomerates, which have a disordered defect structure, while the size of this phase varies over a wide range (Figure 7). In addition, in sample I^{900} , separate, scattered inclusions of nanosized particles of metallic copper with a particle size in the range of 43 to 240 nm with an average size of 81 nm are observed. It should be noted that the copper particles synthesized by the proposed method in the presented sample are characterized by a distorted rounded shape, which may indicate the incompleteness of the particle formation process.



Figure 7. TEM images (a–c) and particle size distribution curve (d) for sample I⁹⁰⁰.

A similar picture is observed for sample II^{900} ; namely, nanosized spherical particles corresponding—according to X-ray powder diffraction results—to the phase of metallic copper, with a particle size in the range of 10 to 73 nm with an average size of 52 nm, and large blocks of irregular shape, corresponding to the boron nitride phase and the amorphous boron phase with a size of 50 nm to 5 μ m (Figure 8).

The difference in the average particle size of samples I^{900} and II^{900} is explained by different reactivities of the chosen precursors $I \cdot nH_2O$ and $II \cdot nH_2O$, namely the inorganic ligand, hydrazine or ammonia. The reactivity of inorganic ligands under thermolysis conditions is different, which clearly affects the time of formation of the final products and their structure. In the case of ammonia (compound $II \cdot nH_2O$) chosen as a precursor, the phase of metallic copper with a particle size in the range of 10 to 73 nm with an average size of 52 nm was obtained. Carrying out the synthesis starting from compound $I \cdot nH_2O$ with a more reactive hydrazine molecule resulted in the preparation of nanosized particles of metallic copper with a particle size from 43 to 240 nm with an average size of 81 nm.



Figure 8. TEM images (a–c) and particle size distribution curve (d) for sample II⁹⁰⁰.

The study of sample I^{900} by high-resolution TEM and EDS made it possible to confirm the earlier conclusions. Figure 9a shows a disordered defective structure of amorphous boron (because of the presence of different orientation planes) and a boron nitride phase are fixed on the surface of copper nanoparticles, the composition of which is confirmed by EDS data for the sample (Figures 9 and 10).



Figure 9. High-resolution TEM image (**a**), TEM image (**b**) and EDS data (copper, boron and nitrogen content) (**c**) of sample **I**⁹⁰⁰.



Figure 10. TEM image (**a**) and EDS data inside the particle (**b**) and the region around the particle (**c**) for sample **I**⁹⁰⁰.

3.5. Electrical Conductivity of Sample I⁹⁰⁰

A suspension of sample I^{900} in ethanol was further used to prepare functional ink, which is a dispersed system suitable for microplotter printing of the corresponding coating on a specialized Pt/Al₂O₃/Pt chip (Figure 11). To increase the sedimentation stability of the dispersed system, it was subjected to ultrasonic treatment for 10 min, after which a glass capillary dispenser was filled with functional ink. Next, ten coating layers were deposited on the surface of the interdigitated platinum electrodes of the chip by microplotter printing. Before applying each subsequent layer, the applied material was dried.



Figure 11. Photo of the Pt/Al₂O₃/Pt chip.

At the next stage, using a constant current source (QJE, PS3003, Ningbo JiuYuan Electronic, Ningbo, China) and a thermal imager (Testo 868), the platinum microheater located on the reverse side of the chip was calibrated. Thus, the dependence of the temperature of the material under study on the voltage applied to the microheater was determined (Figure 12).



Figure 12. Temperature of the studied material vs. voltage applied to the microheater of the $Pt/Al_2O_3/Pt$ chip.

The total electrical conductivity of the sample was determined using the resistance values *R* calculated from the impedance spectra obtained in the temperature range 400–600 °C in the frequency range 1 MHz–1 Hz. The DC resistance R_{DC} was calculated using the following equation:

$$R_{\rm DC} = \lim_{\omega \to 0} Z'(\omega), \tag{2}$$

where *Z*' is the real part of resistance, $\omega = 2\pi f$ and *f* is the frequency.

The values of the specific conductivity of the sample were found from the equation

$$\sigma = \frac{L}{R_{\rm DC} S'}$$
(3)

where *L* is the thickness of the coating under study, and *S* is the coating area.

The activation energy of conduction was calculated using the Arrhenius equation:

$$\sigma = \sigma_0 \cdot \exp\left(-\frac{E_a}{kT}\right),\tag{4}$$

where σ is the electrical conductivity of the sample, σ_0 is the pre-exponential factor, *k* is the Boltzmann constant and *E*_{*a*} is the activation energy of conduction.

As it was found, an increase in temperature leads to a gradual linear increase in the electrical conductivity of sample I^{900} from 1.9×10^{-8} S/cm (400 °C) to 1.1×10^{-5} S/cm (600 °C) (see Figure 13).

It should be noted that the sample preparation process was carried out in air at elevated temperatures, which, in turn, could lead to the oxidation of metallic copper, which is part of the composite. To identify the resulting coating on the chip, an X-ray powder diffraction study was additionally performed. According to X-ray powder diffraction data, along with the reflections of alundum and platinum, as well as the components of the initial composite (cubic BN, cubic Cu), reflections of the cuprite Cu₂O phase are observed in the diffraction pattern (Figure 14).



Figure 13. Specific electrical conductivity of the material under study vs. temperature.



Figure 14. X-ray powder diffraction pattern for sample I⁹⁰⁰ from the chip.

The results obtained indicate that the process of applying the sample to the chip substrate is accompanied by partial oxidation of metallic copper to Cu_2O . These results are in good agreement with the TG-DSC data, which revealed a rather high sensitivity of the annealed sample to air oxygen, which, in turn, is due to nanosized metallic copper.

Note that Cu@BN composites are known to be used in different application fields, including composite reactor materials [46], as heat-resistant and wear-resistant coatings [47], as self-lubricating materials [48], as catalysts [49,50], etc. We hope that the present study will be interesting and useful to chemists working in the field of nanotechnologies, as it fills a gap with a very active area (carbon nanodots and composites) from the organic side.

4. Conclusions

In the course of the study, a method for the synthesis of a boron-containing copper composite Cu@BN based on the thermal reduction of copper(II) complexes with easily leaving ligands $[Cu^{II}(N_2H_4)_3][B_{10}H_{10}] \cdot nH_2O$ (I· nH_2O) and $[Cu^{II}(NH_3)_4][B_{10}H_{10}] \cdot nH_2O$ (II· nH_2O) in an argon atmosphere up to 900 °C was proposed. It has been found that this thermal reduction process is accompanied by copper(II) \rightarrow copper(I) \rightarrow copper(0) reduction due to the presence of inorganic components (NH₃, N₂H₄, the *closo*-decaborate anion $[B_{10}H_{10}]^{2-}$) that exhibit reducing properties. Based on the data from X-ray powder diffraction, IR spectroscopy and thermal analysis, the compositions and structures of annealing products I^{900} and II^{900} were identified; in the annealing products, a cubic boron nitride phase doped with cubic copper(0) nanoparticles was detected. These conclusions are confirmed by the study of the morphology of the annealing products by TEM, as well as high-resolution TEM + EDS for sample I^{900} . An express test of the electrical conductivity of the fabricated coating based on the I^{900} sample modified in situ during deposition on a chip at 300 °C showed an increase in the electrical conductivity characteristic of semiconductors with increasing temperature.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/inorganics11080345/s1, Figure S1: X-ray powder diffraction pattern for I^{900}_{Ar} (b) and II^{900}_{Ar} (a); 1–copper (cubic system), 2–BN (cubic system).

Author Contributions: E.A.M.: Conceptualization, Writing—Original Draft; I.I.M.: Investigation, Formal analysis; G.A.B.: Formal analysis, Visualization; I.V.K.: Formal analysis, Visualization; N.P.S.: Formal analysis, Visualization; T.L.S.: Formal analysis, Validation; S.E.N.: Methodology, Writing—review and editing; V.V.A.: Conceptualization, Writing—review and editing; K.Y.Z.: Project administration; N.T.K.: Supervision. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. The authors declare that they have no conflict of interest.

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