Modification of the valence band electronic structure under Ag intercalation underneath graphite monolayer on Ni(111)

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Abstract

Angle-resolved photoemission spectroscopy and Auger electron spectroscopy have been applied to study the intercalation process of silver underneath a monolayer of graphite (MG) on Ni(111). The room-temperature deposition of silver on top of MG/Ni(111) system leads to the islands-like growth of Ag on top of the MG. Annealing of the "as-deposited" system at temperature of 350-450° C results in the intercalation of about 1-2 ML of Ag underneath MG on Ni(111) independently of the thickness of pre-deposited Ag film (3-100 Å). The intercalation of Ag is followed by a shift of the graphite-derived valence band states towards energies which are slightly larger than ones characteristic for pristine graphite. This observation is understood in terms of a weakening of chemical bonding between the MG and the substrate in the MG/Ag/Ni(111) system with a small MG/Ni(111) covalent contribution to this interaction.
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I. INTRODUCTION

The continuing interest in carbon-based material has resulted in a number of studies of their magnetic, electronic, and transport properties which are interesting from technological as well as fundamental point of view [1, 2]. The ability to alter the properties of graphite and graphite intercalation compounds (GICs) makes them interesting candidates for a range of applications including, for example, magnetic storage, hard coating, and optical devices. Also, quasi-two-dimensional or even one-dimensional character of mentioned structures gives the opportunity to use them as model systems for different studies in solid-state physics and chemistry.

In the last decades the systems on the basis of noble metals (Cu, Au, Ag) intercalated underneath a monolayer of graphite (MG) on top of Ni(111) were extensively investigated by means of high-resolution-electron-energy-loss-spectroscopy (HREELS) [3–6] and photoemission spectroscopy (PES) [6, 7] methods. These systems have attracted a strong interest due to a quasi two-dimensional geometric and electronic structure. In these noble metal intercalation-like systems an unusual effect of energetic shift of graphite-derived branches in the valence band electronic structure and the phonon vibration spectra after intercalation of noble metals were observed. This effect is caused by the weakening of the "MG-substrate" interaction due to the noble metal intercalation. From the other side, this intercalation-like system on the basis of MG and noble metal can be chosen as a possible way of formation of a flat layered structure, in spite of the case of noble metal deposition on pure Ni(111) surface, where the formation of three-dimensional island-like structures was observed. In particular, in work [8] the formation of flat pseudomorphic copper layer on top of Ni(111)
was possible by using a benzene as surfacant with subsequent removing of benzene from the surface after intercalation process.

In this paper the investigations of the valence band electronic structure modification upon Ag intercalation underneath MG located on top of the Ni(111) by angle-resolved photoemission spectroscopy (ARPES) are presented. This work is a continuation of HREELS-investigations of this system [5]. In spite of our previous PES investigations of the analogous systems on the basis of copper and gold as intercalant [6,7], in the current work, the attention was attracted to the changes in the graphite-derived electronic structure as well as to estimation of amount of intercalated Ag as a dependence of the annealing temperature as well as of the amount of deposited Ag on top of MG/Ni(111) system.

The present investigations show that the most appropriate temperature for intercalation of Ag atoms underneath MG on Ni(111) is in the range between 350 and 400-450°C. Above these temperatures the partial system degradation was observed. As a result of Ag atoms intercalation at 350-450°C the energetic shift of the graphite-derived valence band states was observed. In this case these branches are located at lower binding energies in comparison with the MG/Ni(111) system that can be explained by the weakening of the "MG-substrate" interaction after Ag intercalation underneath MG.

As it was mentioned above one of the present work tasks was determination of the intercalated amount of Ag underneath MG on top of Ni(111). In the recent works [9,10] the process of Ag atoms intercalation underneath MG on Ir(111) textured foil was investigated. Auger electron spectroscopy (AES) and thermo-desorption spectroscopy (TDS) investigations showed that maximal amount of Ag which can be intercalated underneath MG is one monolayer (ML) in contrast to the Ag concentration deposited on top of MG. Earlier in our
previous work [5] the assumption about intercalation of only 1 ML of Ag underneath MG and that the rest of deposited Ag formed a large 3D islands on top of MG/Ni(111) system was made.

To make this problem clear in the present work the AES experiments for three different amount of pre-deposited Ag (3, 10 and 100 Å) were performed. For estimation of Ag intercalated amount the mean free path of AES electrons should be taken into account. In this case for careful analysis of the intercalation process the high kinetic energy ($E_{kin}$) AES lines of elements were chosen. As a result of AES investigations the amount of Ag intercalated underneath MG was estimated to about 2 ML independently on thickness of pre-deposited amount of Ag (3-100 Å). This value is very small in comparison to the amount of Ag deposited on the sample surface before the intercalation. In this case the formation of large 3D islands of non-intercalated Ag is expected.

II. EXPERIMENTAL DETAILS

The experiments were carried out in two separated UHV experimental chambers equipped with low energy electron diffraction (LEED) and AES optics, an ion gun and a gas inlet system. Angle-resolved photoemission measurements were carried out with ADES-type spectrometer at the Berliner Electronenspeicherring für Synchrotronstrahlung (BESSY I, Berlin, Germany) using a monochromatic light with the photon energy of 50 eV from TGM2 beamline. Total energy resolution was 100 meV and angle resolution was 1°. The AES experiments were carried out by four-grid electron spectrometer with relative energy resolution of 0.25%. All spectra were collected in $dN/dE$ mode with energy of primary electron beam of 1000 eV.
and modulation voltage of 2 V. The base pressure in the experimental chambers was better than $1 \times 10^{-10}$ mbar.

MG was formed on top of the Ni(111) surface by cracking of propylene ($C_3H_6$) at surface temperature of 500°C using the recipe described in details in [3–7]. Sample exposition at a propylene pressure of $1 \times 10^{-6}$ mbar during 4 min was enough to form a well ordered MG layer on top of Ni(111) surface. The crystallographic structure was checked by LEED and ordered hexagonal LEED picture with three-fold symmetry was observed [3–7]. Ag films were deposited at room temperature from melted Ag piece (purity 99.9%) supported by W wire which was heated by current and thickness of the deposited layer was simultaneously measured by water-cooled quartz microbalance monitor. The processes of Ag intercalation underneath MG on top of Ni(111) surface was investigated at a substrate temperature in the range between 350 and 500°C. Same sample preparation procedure of the intercalation-like system on the basis of Ag and MG was described earlier in our work [5] for HREELS investigations of the phonon structure of MG/Ag/Ni(111) system.

III. EXPERIMENTAL RESULTS AND DISCUSSION

In Fig.1 a series of the normal emission valence band photoemission spectra is presented for "as-deposited" 100 Å-thick Ag-overlayer on top of the MG/Ni(111) system as well as after annealing of the (Ag + MG/Ni(111)) system at different temperatures in the range between 350 and 500°C. These temperature regimes are appropriated for Ag-intercalation in accordance with our previous HREELS investigations [5]. For comparison, the corresponding spectrum for the initial MG/Ni(111) system is shown by open symbols.
PES spectrum for the MG/Ni(111) system is characterized by pronounced $\pi_{1v}$ and $\sigma_{2,3v}$ graphite-derived features located at the binding energies (BE) of about 10.2 and 5 eV, respectively, and two Ni 3$d$-derived features with maxima at 0.5 and 1.4 eV BE. Room-temperature deposition of 100 Å Ag leads to suppression of MG- and Ni-derived states in the PES spectra. The dominant features in the spectra are Ag 4$d$-derived states located in the BE range between 4 and 7 eV. Despite a significant amount of deposited Ag (about of 100 Å) the weakened Ni 3$d$ states at the BE of 0.5 and 1.5 eV and very weak $\pi_{1v}$ graphite-derived features at about of 10 eV can be distinguished in the spectra that can testify an island-like character of "as-deposited" Ag-layer. Additional feature observed at the Fermi-level ($E_F$) can be related to the surface states characterized for metallic silver [12].

Annealing of the 100 Å Ag/MG/Ni(111) system at 350° C is followed by the restoring of the $\pi_{1v}$ graphite-derived states and disappearing of the Ni 3$d$ states in the energy region between $E_F$ and 1.5 eV BE. In comparison with the initial MG/Ni(111) system the $\pi_{1v}$ graphite-derived states are shifted towards lower BE by of 1.3 eV up to of about 9 eV BE. The Ag 4$d$-derived features remain dominant ones in the PES spectra. Increase of annealing temperature up to 400 and 450° C leads to further decreasing of the BE of $\pi_{1v}$-derived states. After annealing at 450° C the BE of the $\pi_{1v}$ graphite-derived states reaches the value of about 8.3 eV relative to $E_F$. Further increase of annealing temperature up to 500° C is followed by reverse increasing of the BE of the $\pi_{1v}$-derived states. The structure of the Ag 4$d$-derived states does not changed at these annealing temperatures. The restoring of the intensity of $\pi_{1v}$ graphite-derived states and the decreasing of their BE after annealing of the Ag/MG/Ni(111) system at temperatures above than 350° C can be explained by the intercalation of Ag atoms underneath MG on top of Ni(111) and the change of the "MG-substrate" interaction after
intercalation.

In Fig. 2 the changes of the relative intensities of the $\pi_{1v}$ graphite-derived states at 10.2 eV BE and the Ag 4$d$-derived feature located at 4.5 eV BE are presented for the annealed system at different temperatures in comparison with those for the MG/Ni(111) system and for the "as-deposited" Ag overlayer on top of MG/Ni(111) system. It can be seen that annealing at $350^\circ$C leads to a growth of the intensity of the $\pi_{1v}$ graphite-derived feature and suppression of the intensity of the Ag 4$d$-derived one. Increase of the annealing temperature up to 400 and 450$^\circ$C leads to the further increasing of the intensity of the $\pi_{1v}$ graphite-derived states and suppression of the Ag 4$d$-derived states. However, annealing at temperature of 500$^\circ$C is followed by the decreasing of intensity of the $\pi_{1v}$ graphite-derived states as well as by the increasing of the Ag 4$d$-derived ones.

On the basis of the presented data (changes of the BEs and of the intensity of the graphite- and Ag 4$d$-derived states) the optimal temperature for the Ag-intercalation in the range between 350 and 450$^\circ$C was found. At higher annealing temperature leads to the start of the MG/Ag/Ni(111) system degradation process was observed.

In order to estimate the quantity of intercalated Ag underneath MG on top of the Ni(111) surface the AES experiments were carried out. Three different thicknesses of Ag were used (3, 10 and 100 Å). The AES intensities of the C(KVV), Ag(M$_5$N$_{45}$N$_{45}$), Ni(L$_3$M$_{45}$M$_{45}$) and Ni (MVV) lines with $E_{\text{kin}}$ = 272, 351, 848, and 60 eV respectively, depending on annealing temperature for the case of 100 Å of pre-deposited Ag on top of MG/Ni(111) system are shown in Fig. 3a. The choice of these lines for quantitative analysis was caused by the possibility to carefully separate the contributions from different elements (C, Ag and Ni) and by the reason that the electrons with such kinetic energy have a larger mean free path than
electrons with $E_{\text{kin}}$ around 50 eV analysed in PES experiments. Encircled numbers I and II in Fig.3a correspond to MG/Ni(111) system and system after deposition of corresponding amount of Ag on top of MG, respectively. After Ag deposition the intensities of the C and Ni AES peaks decreased and Ag AES peak increased. After annealing of the Ag/MG/Ni(111) system the situation is changed: intensity of the Ag AES peak is decreased and intensities of the carbon and Ni peaks are increased. At annealing temperature of about 300° C the intensity of carbon peak is the same as for the MG/Ni(111) system. In this case the situation is following: the graphite layer is on the top of the system and Ag intercalation underneath MG on top of Ni(111) takes place. In the same time the Ni AES peak has a visible intensity at least three times smaller in comparison with the MG/Ni(111) system.

For comparison, the changes of the intensity ratio of the Ni and Ag AES peaks with temperature change are presented in Fig.3b and marked by solid squares, circles and triangles for 3, 10 and 100 Å of pre-deposited Ag, respectively. For systems with 3 and 10 Å of pre-deposited Ag on top of the MG/Ni(111) the behaviours of the AES spectra with changes of annealing temperature are the same (not shown here): decreasing of the intensity of the carbon and Ni AES peaks after deposition of Ag and increasing ones after annealing at temperatures above 250° C. For all three cases the intensity of the carbon AES peak for the system, which is produced by the annealing of the Ag/MG/Ni(111) system at 350-370° C, is nearly the same and has an intensity comparable with intensity of carbon AES peak for the MG/Ni(111) system. In all cases the Ni AES peaks were also observed. From the analysis of the Fig.3a and 3b the main features can be pointed: (i) intensity of the Ni AES peak for the case of 100 Å pre-deposited Ag after annealing procedure is two times smaller than for the case of 3 Å pre-deposited Ag, where intercalation of 1 ML of Ag was supposed, (ii) for the
system with 100 Å of pre-deposited Ag the intensity of the Ni AES peak after annealing is decreased by three times in comparison with MG/Ni(111) system, (iii) for all three systems the Ni AES peak with kinetic energy of 60 eV is clearly visible (this peak has a small inelastic mean free path in comparison with other AES peaks). On the basis of this analysis one can conclude that for all three cases of pre-deposited Ag on top of MG/Ni(111) system, only about 2 ML of Ag can be intercalated underneath MG on top of Ni(111) independently on thickness of pre-deposited Ag film. This conclusion is in a good agreement with results of works [5,9,10] where the thickness of intercalated Ag was estimated as 1 ML, but near some imperfections of the surface of the Ni crystal (as a defects, steps, dislocations etc.) the intercalations of two or more monolayers of Ag can be expected.

For analysis of the peaks intensities extracted from PES data the mean free path of photoelectrons at $h\nu=50$ eV has to be taken into account. From these estimations of the intensity changes of Ni 3$d$ states near $E_F$ one can conclude that 2-3 MLs of covered layer on top of Ni(111) (together with MG) should be enough to completely depress the intensity of these states near $E_F$. These estimations together with presented AES data lead to a conclusion that in case of Ag intercalation underneath MG only 1-2 monolayers of Ag are intercalated underneath MG matrix. The rest of Ag can decorate the defects at the surface and form a randomly-situated large 3D-islands as a lot of dislocations were observed by STM on MG surface as it was shown in previous investigations of copper intercalations underneath MG [7]. The next possibility is the agglomeration of Ag at the borders of the sample. This estimation can be compared with the results of work [6,7]. In case of Au the 1 ML intercalation underneath MG on top of Ni(111) the Ni 3$d$ states near $E_F$ were also
fully depressed. In opposite, for Cu intercalation the Ni 3d states still can be distinguished. Such differences in the Ni 3d states behaviour for the noble metal intercalation underneath MG on Ni(111) can be explained by the nickel-copper alloy formation and absence of such alloys for Au and Ag at temperatures essential for noble metal intercalation.

In Fig.4 a series of angle-resolved PES spectra for the MG/Ag/Ni(111) system formed by annealing of 100 Å Ag+MG/Ni(111) system at 450° C are presented. Spectra were measured in Γ-K direction of the graphite surface Brillouin zone (SBZ). Corresponding dispersions of the main valence band graphite-derived electronic states are shown in Fig.5 for the systems formed by annealing at temperatures of 350, 400 and 450° C. Also in Fig.5 the dispersion in Γ-M direction for the MG/Ag/Ni(111) system with the 3 Å and 4.7 Å of the pre-deposited Ag is shown by open squares and circles, respectively. The measurements in this case were made with the He resonance lamp and photon energy was 40.8 eV. Here, for comparison the dispersion of the \( \pi \) and \( \sigma \) graphite-derived states for the MG/Ni(111) system as well as for pristine graphite are shown by straight and dash-dotted lines, respectively. Similar to Fig.1 the PES spectra presented in Fig.4 are characterized by dominant contribution of the Ag 4d-derived features. The fine structure of the Ag 4d-derived states practically do not changed with the polar angle variation. These states are practically non-dispersive in the PES spectra. Besides the Ag 4d-derived structure the PES spectra are characterized by the \( \pi_{1v} \), \( \sigma_{1v} \) and \( \sigma_{2,3v} \) graphite-derived states with strong dispersion. Binding energy of the \( \sigma_{1v} \) and \( \pi_{1v} \) states in the Γ point of the SBZ (normal emission) are equal to 21.5 and 8.3 eV, respectively. By increase of the polar angle the \( \pi_{1v} \)-states reach the position with the BEs lower than those for the Ag 4d-derived states. For polar angles over 25° (\( k_\parallel >1.4-1.5 \text{Å}^{-1} \)) the \( \pi \)-states are split in two features. One feature reaches the BE of about
3 eV for \( k_{\parallel} \approx 1.5 \, \text{Å}^{-1} \). Second feature has the lowest BE equals of about 1 eV for the polar angles in the region of 30° \( (k_{\parallel} = 1.7 \, \text{Å}^{-1}) \) that corresponds to the \( \overline{K} \) point of graphite SBZ. By further increase of polar angle both states show decreasing intensities and shift towards higher BEs. Besides the \( \pi_{1v} \) and \( \sigma_{1v} \) graphite-derived states, the \( \sigma_{2,3v} \) graphite-derived states can be distinguished in the PES spectra for polar angles over 20° (Fig.5). These states are also strongly dispersive. Dispersive dependencies for these states are presented in Fig.5. In comparison with the dispersion dependencies of the MG/Ni(111) system the branch of the \( \pi_{1v} \) graphite-derived states is significantly shifted as whole towards lower BEs by about of 1.5-2 eV after intercalation of Ag atoms underneath MG on Ni(111). In the \( \overline{K} \) point of the graphite SBZ the BE of the \( \pi_{1v} \) states for the MG/Ag/Ni(111) system is about of 1 eV in comparison with the BE about of 3 eV for the MG/Ni(111) system. Totally the \( \pi_{1v} \) states for the MG/Ag/Ni(111) system are located in the region between branches characteristic for pristine graphite and for the MG/Ni(111) system. In the region of the \( \overline{K} \) point they are located more close to the positions characteristic for pristine graphite. The \( \sigma_{1v} \) states in the region of the \( \Gamma \) point are located at the energy characteristic for pristine graphite. In the region of the \( \overline{K} \) point these states have the BE about of 16.5 eV. This energetic shift of the graphite-derived valence band states for the MG/Ni(111) system can be attributed to weakening of the interaction of MG with Ni-substrate after intercalation of Ag atoms. In accordance to [13,14] this interaction for the MG/Ni(111) system is caused by orbital mixing (hybridization) of the \( \pi \)-states of MG with 3\( d \)-states of the substrate. Such hybridization is followed by electron redistribution from the bonding \( \pi \)-states to antibonding \( \pi^* \)-states that results in the weakening of the (C-C) bonds in the graphite layer and increase of the BE
of the graphite-derived states (different for the $\sigma$ and $\pi$ states). Intercalation of Ag atoms increases the distance between MG and Ni-substrate and, as consequence, leads to decreasing of the MG $\pi$ - Ni 3$d$ interaction and to significantly lower BEs of the $\pi$ and $\sigma$ graphite-derived states as compared to those in the MG/Ni(111) system. The assumption about the weakening of the "MG-substrate" interaction after Ag-intercalation is in agreement with the results of HREELS investigations of the MG/Ag/Ni(111) system [5] which displays the analogous effect of "stiffening" of the graphite-derived phonon modes after Ag-intercalation.

In some degree analogous energetic shift of the graphite-derived states were recently observed upon intercalation of gold and copper underneath MG on the Ni(111) [6,7]. But in that case the $\pi$ and $\sigma$ graphite-derived states were shifted upon Cu or Au intercalation up to the positions characteristic for pristine graphite. Such difference between modification of the PE spectra upon intercalation of Ag, Cu and Au can be explained by more complex interaction of Ag with MG and Ni-substrate. According to results of Oshima et al. calculations of the phonon modes in the MG/Cu/Ni and MG/Ag/Ni systems the interaction of MG with substrate after intercalation of Ag is more stronger than that, which realizes in the case of pristine graphite and the Mg/Cu/Ni(111) system [15].

On the basis of these experimental observations the following model can be proposed: after intercalation of Ag in the MG/Ni(111) system the covalent-like nature of interaction between MG and substrate is saving due to the (Ni - Ag) interaction. However, the strength of this interaction is lower than in the case of the MG/Ni(111) system. This assumption is supported by the experimental fact, which shows that the occupation of the $\pi^*$ graphite-derived states and the appearance corresponding features in the PES spectra were not observed. This situation is opposite to the case of the alkali metal intercalation
underneath MG where these effects were observed [13].

Other interesting effect observed after the Ag-intercalation is the splitting of the $\pi$ graphite-derived states in the PES spectra for polar angles over $25^\circ \ (k_{||} > 1.4 \ \text{Å}^{-1})$. In our opinion the observed difference in the energetic positions and the angle dependencies of both $\pi$ graphite-derived branches maxima can be related to different behavior of the $\pi$ states in the regions of the $\overline{K}$ and $\overline{M}$-point of the graphite SBZ. On this basis one can assume that the second branch of the $\pi$ states with maximum of the BE at $4 \ \text{eV} \ at \ k_{||} \sim 1.4 \ \text{Å}^{-1}$ is similar to the behavior of the $\pi$ states in the region of the $\overline{M}$-point of the SBZ, i.e. it can be the "footprint" of the $\overline{\Gamma} - \overline{M}$ direction (see, for comparison, the real dispersion in $\overline{\Gamma} - \overline{M}$ direction shown by open symbols). It can be caused by some domains disorientation in graphite monolayer which can arrive after Ag atoms intercalation. The BE value of the $\sigma_{1\nu}$-states observed in the region of the $\overline{K}$-point of the SBZ can be also understood from analogous positions. This part of the $\sigma_{1\nu}$ graphite-derived branch can be also related to "footprint" of the $\sigma_{1\nu}$ states in the $\overline{\Gamma} - \overline{M}$ direction. The LEED pattern of the system after Ag atoms intercalation displays graphite-like (1×1) hexagonal structure characteristic for the MG/Ni(111) system with some weak strips rotated on $15^\circ$ with respect to hexagonal ones. Such LEED patterns suggest that the prepared system is terminated by graphite-like domains with some orientation misfit with respect to the Ni(111) substrate, as it has been already observed for the MG/Cu/Ni(111) system [3,4] and has been described for the MG/Ag/Ni(111) system [5]. This disorientation is ordered one that leads to equivalent electronic structure both in the $\overline{\Gamma} - \overline{K}$ and $\overline{\Gamma} - \overline{M}$ directions of the monocrystalline graphite SBZ. From the other side the splitting of the $\pi$ graphite-derived states for the MG/Ni(111) system around $\overline{K}$-point of the graphite SBZ was theoretically predicted by Souzu et al. [16]. The energy dispersion of the


\(\pi\) graphite-derived states along the high-symmetry line \(\Gamma - \bar{K} - \bar{M}\) has a splitting-point at around of 2 eV BE. But for the isolated graphene layer which can be taken as an ideal case in the model of MG/Ag/Ni(111) intercalation-like system this splitting-point lies at \(E_F\) [16]. The possible energy shift can be caused by the rest interaction MG with substrate and deviation from the ideal model of isolated graphene layer.

IV. CONCLUSION

On the basis of the PES and AES investigations of the Ag intercalation process underneath MG on top of the Ni(111) surface the following conclusions can be made: (i) optimal temperature for intercalation of Ag underneath MG lies in the range 350-450°C; at temperature above 500°C the degradation of the MG/Ag/Ni(111) system starts; (ii) the valence band electronic structure of the MG/Ag/Ni(111) system is characterized by the energetic shift of the \(\pi\) and \(\sigma\) graphite-derived states as compared with the MG/Ni(111) system towards lower BEs by about of 1.5-2 eV and 0.5-1 eV, respectively; it is assumed that the observed changes of electronic structure is caused by the weakening of the \(\pi-d\) interaction of the MG with substrate; the "orbital mixing" nature of this interaction is saving after Ag intercalation; (iii) on the basis of intensity changes analysis of C, Ag and Ni AES peaks in intercalation process a conclusion about 1-2 ML of intercalated Ag underneath MG on top of Ni(111) was made and this value practically independent from the amount of Ag deposited on top of the MG/Ni(111) system before intercalation; after intercalation of 1-2 ML of Ag the formation of the large Ag islands which have a total square less than 50% of the surface can be expected; the agglomeration of the Ag at the surface dislocations and border of the
sample can not be excluded.

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**Fig.1.** PES spectra of the MG/Ni(111), 100 Å of Ag on MG/Ni(111), as well of Ag/MG/Ni(111) system after annealing at 350, 400, 450 and 500° C, respectively.

**Fig.2.** The changes of relative intensities of the $\pi_{1v}$ graphite-derived state and the Ag 4$d$-derived feature after annealing of the Ag/MG/Ni(111) system at different temperatures in comparison with those for the MG/Ni(111) system and for the ”as-deposited” Ag overlayer on top of MG/Ni(111) system.

**Fig.3.** a) Intensity of the C(KVV), Ag(M$_5$N$_{45}$N$_{45}$), Ni(L$_{3}$M$_{45}$M$_{45}$) and Ni(MVV) AES peaks in dependence from the annealing temperature for 100 Å of pre-deposited Ag on top of MG/Ni(111) system. b) temperature dependence of the intensity ratio $(I(\text{Ni}_{848}))/I(\text{Ag}_{351}))$ for different amount of pre-deposited Ag on top of the MG/Ni(111) system.

**Fig.4.** Series of the angle-resolved PES spectra measured at photon energy of 50 eV for the MG/Ag/Ni(111) system formed after annealing of 100Å Ag+MG/Ni(111) system at 450° C.

**Fig.5.** Dispersion plot of the main valence band graphite derived electronic states for the Ag/MG/Ni(111) system formed after annealing of 100 Å Ag+MG/Ni(111) system at temperatures of 350 (up triangles), 400 (down triangles) and 450° C (diamonds). The experimental data points for the $\Gamma$ – $\overline{M}$ direction and photon energy 40.8 eV are shown by open symbols. Here, for comparison the dispersion of the $\pi$ and $\sigma$ states for the MG/Ni(111) system as well as for pristine graphite are shown by straight and dash-dotted lines, respectively.