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Interface formation in the Gd/HOPG and Dy/HOPG systems Electron spectroscopy studies

S.I. Bozhko[a,*], A.N. Chaika[a], A.M. Ionov[a], U. Valbusa[b]

[a]*Institute of Solid State Physics RAS, Chernogolovka, Moscow District, 142432, Russia*
[b]*INFM and Physics Department, University of Genoa, Via Dodecaneso 33, 16146 Genoa, Italy*

Abstract

The electronic and atomic structures of the interfaces formed upon deposition of Gd and Dy onto HOPG(0001) at substrate temperatures of 20 and 300 K have been studied by AES, UPS, XPS, EELS, and LEED. At both temperatures studied, Gd/HOPG interface reproduces atomic structure of HOPG(0001) up to 20 Å thicknesses. The analysis performed by AES favors a quasi layer-by-layer growth and diffusion of Gd and Dy into interplane space of graphite even at 20 and 300 K. The structure of Dy/HOPG interface is different from that of the Gd/HOPG system: at thick coverages (45 Å) when only Dy features are observed by electron spectroscopy, the LEED pattern typical of clean HOPG(0001) coexists with superstructural rings. Annealing of the interfaces at temperatures up to 1300 K induces, most probably, formation of the ordered carbide-like systems with geometrical structure analogous to that of pristine graphite for Gd-C and superstructure of $\sqrt{3}\times\sqrt{3}$ type for Dy-C systems. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Surfaces and interfaces; Electron energy loss spectroscopy; Photoelectron spectroscopy; LEED

1. Introduction

In the last few years, graphite has attracted considerable interest [1–3] mainly due to its layered quasi-two-dimensional structure. This fact enables the use of graphite as a matrix for creation of ordered subsystems with unique magnetic and transport properties. From this point of view low-dimensional ordered structures based on rare earth (RE) metal–graphite compounds are of major practical and theoretical importance. Heavy REs (Gd, Dy) with large spin are good candidates for the formation of compounds with interesting physical properties, in particular magnetic and electronic ones.

We report on a study of the electronic and atomic structures of the Gd and Dy–graphite systems performed by Ultra-violet Photoelectron Spectroscopy (UPS), X-ray Photoemission Spectroscopy (XPS), Auger Electron Spectroscopy (AES), Electron Energy Loss Spectroscopy (EELS), and Low Energy Electron Diffraction (LEED).

2. Experimental

Samples of highly oriented pyrolytic graphite (HOPG) were cleaved at atmospheric pressure and then annealed at temperatures up to 1300 K in ultra high vacuum (UHV) at pressures lower than 1×10^{-8} Torr. Gd and Dy were evaporated onto the HOPG substrate at 20 K and 300 K from W spiral in the UHV chamber with a base pressure of 1×10^{-10} Torr. Increase in the pressure during deposition did not exceed 2×10^{-9} Torr. The purity of the interfaces was checked by monitoring oxygen AES signal after each deposition. The thickness of deposited Gd and Dy was monitored by a quartz microbalance with an accuracy of 20%. One monolayer (ML) of Gd and Dy coverage corresponds to 3.2 Å.

Experiments were performed using the electron spectrometer ESCALAB-5 with a spherical sector analyzer. The energy resolution was 0.2 eV for UPS, 0.1 eV for low

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*Corresponding author. Tel.: +7-095-962-8091; fax: +7-096-576-4111.

E-mail address: bozhko@issp.ac.ru (S.I. Bozhko).

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(60 eV) and 0.5 eV for higher (1100 eV) electron energy loss spectroscopy. Photoemission experiments were carried out using He discharge lamp ($h\nu = 21.2$ and 40.8 eV) and Al K_α X-ray source ($h\nu = 1486.6$ eV).

3. Results and discussion

Investigations of the atomic structure of the cleaved HOPG crystals by LEED showed diffraction patterns (rings) typical of clean (0001) surfaces (see Fig. 1a). During Gd deposition, the LEED pattern with concentric rings was monitored up to 6–7 ML coverage. At coverages higher than 4 ML, Gd deposition induced appearance and growth of a diffuse background in the LEED pattern. At coverages close to 10 ML and higher, only the diffuse background remained indicating the formation of a disordered Gd overlayers. Subsequent annealing at 900 K and higher temperatures (up to 1300 K) led to recovery of the ring-like LEED pattern with the same structure as in pristine graphite. LEED studies of the Dy/HOPG system showed that the image typical of clean HOPG(0001) persists up to 5 ML coverage. At higher coverages ($\theta = 7$ ML), a pattern shown in Fig. 1b was observed. Since both LEED pictures (Fig. 1a and b) were taken at the same incident electron beam energy ($E_p = 62$ eV) we can assume $\sqrt{3} \times \sqrt{3}$ structure for the Dy/HOPG interface at high coverages (up to 14 ML). This structure was observed after annealing of the Dy/HOPG system at different temperatures (600–1300 K).

AES spectra of the Gd, Dy/HOPG systems shown in Fig. 1 (lines 1–8) demonstrate the evolution of the

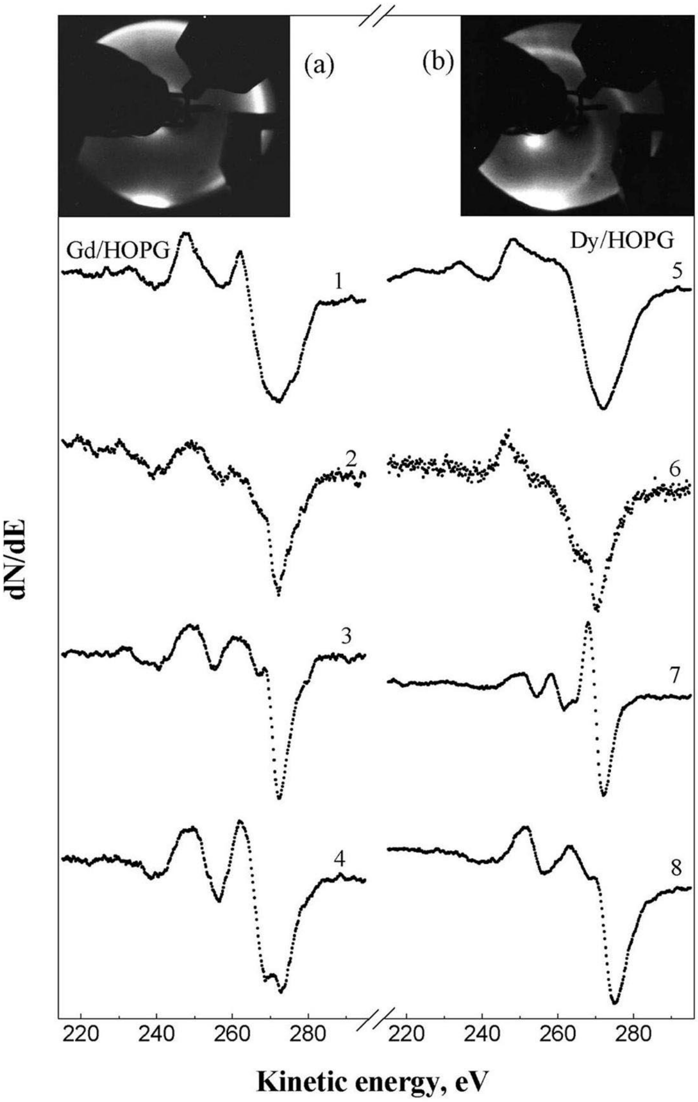

Fig. 1. LEED pattern of the Gd/HOPG system at 4 ML (a) and Dy/HOPG interface at 7 ML coverage (b). Both images were taken at incident electron beam energy $E_p = 62$ eV. C(KVV) AES spectra of the Gd, Dy/HOPG systems: 1, 5: clean HOPG; 2, 6: HOPG+7 ML of Gd and Dy; 3, 7: annealing at 1000 K; 4, 8: annealing at 1300 K. The Gd/HOPG and Dy/HOPG systems were annealed at 40 and 45 Å coverages, respectively.

C(KVV) peak shape. Deposition of Gd and Dy onto the HOPG(0001) did not affect noticeably the shape of the C(KVV) spectrum at the initial stages (up to 5 ML). One can observe slight modification of the C(KVV) lines already after deposition of 6 ML of Gd and Dy (2, 6) and remarkable changes after annealing of the interfaces (3, 4, 7, and 8). Similar AES spectra were observed earlier for carbides of some transition metals [2,4,5]. The absence of the feature near 280 eV [6] attributed to intercalated graphite seems to indicate that temperatures of annealing higher than 1300 K are needed for the formation of Gd and Dy intercalated graphite.

Attenuation curves obtained for the C(KVV) signal (Fig. 2) demonstrated similar behavior at 20 K and 300 K. As an example, C(272 eV) Auger-signal amplitude as a function of Gd and Dy coverage at room temperature is shown in Fig. 2a. A quasi-layer-by-layer character of the Gd growth may be suggested from the almost exponential attenuation of the substrate signal. At the same time, the attenuation of the C(KVV) signal is not so rapid as could be expected from ideal layer-by-layer growth [7] and has some deviations from the exponential decay.

Fig. 2b shows the result of more detailed profile analysis of the C(KVV) AES signal attenuation at the first stages of the Gd growth (0–4 ML). The attenuation curve exhibits kinks at coverages close to 1, 2, and 3 ML imposed on the nearly exponential decay. We suggest that these kinks as well as slow attenuation rates obtained for the C(KVV) Auger signal are caused by interdiffusion of Gd an Dy atoms into the bulk of HOPG after completion of the previous ordered monolayer and formation of the layered structure (Gd-C-Gd-C-Gd-C-C-C). Note that similar non-monotonous behavior of C(272) and Ru(231) AES signals in the vicinity of 1 ML of Ru coverage were observed in Ru/C(0001) system [8].

The EELS spectra of pristine graphite (bottom lines in

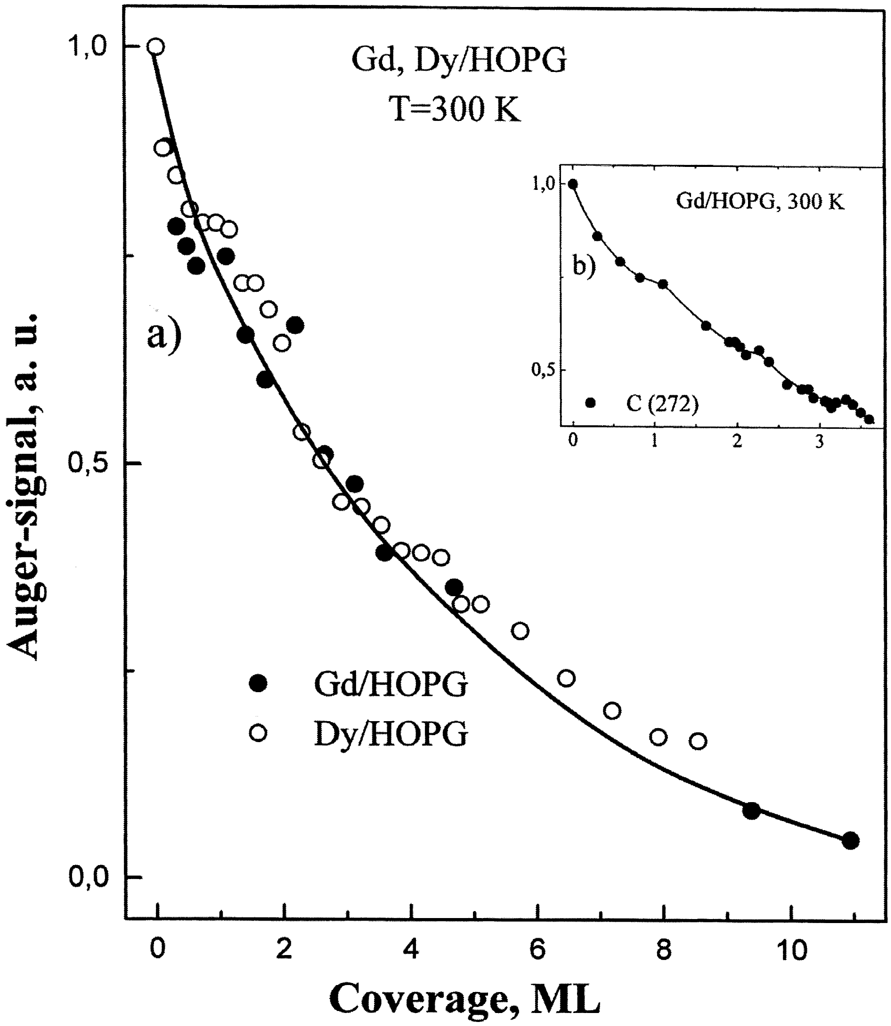

Fig. 2. Amplitudes of C(272) AES signal measured as peak-to-peak heights as a function of Gd and Dy coverage during the interface formation (a) and profile analysis of the attenuation of C(KVV) signal at the initial stages (up to 4 ML) of the Gd deposition (b). Solid lines in the spectra are guide to the eyes.

Figs. 3, 4) exhibit two main broad features with the maxima at about 27 eV and 7.5 eV corresponding to the bulk and π-plasmons. After Gd and Dy deposition, the sp^2- and π-plasmon peaks weaken and new losses arise at the lower energy side. At high coverages, sharp electronic transitions in the 3–8 eV range are well pronounced. These losses are caused by optically forbidden and nonforbidden *f–f* transitions. A multiplet structure with the main peak at 4.5 eV appears after the deposition of Gd and subsequent annealing of the Gd/HOPG system. These peculiarities in the loss spectra may be associated with spin–flip excitations from the ground state $^8S_{7/2}$ to excited ^6X_j multiplet [9–12]. Good agreement in the energy position and intensity of the *4f–4f* losses, their sharpness and insensitivity to the chemical environment confirm the quasiatomic character of *4f* electrons in Gd and Gd compounds (see, for example, the multiplet structure obtained for GdS [13]).

In the spectra of the clean HOPG(0001) surface taken at primary electron beam energy of 1100 eV shown in Fig. 5 (bottom curves) two main features correspond to the plasmon excitations (27 and 6.7 eV, respectively). The increase in Gd and Dy coverage leads to the appearance of the *5p–5d* resonance excitation peaks (35 and 37 eV for Gd and Dy, respectively) and bulk plasmons at 12–13 eV. The intensity of π-plasmon (6.7 eV) in the high energy ELS spectra decreases during deposition. However, the π-plasmon is still visible up to 5 ML of Gd coverage, whereas in the low energy ELS spectra this plasmon peak disappears completely at 2 ML coverage that is related to higher surface sensitivity of EELS at lower primary energies. For the Dy/HOPG interface, π-plasmon in high energy ELS spectra could be observed even at coverages higher than 5 ML.

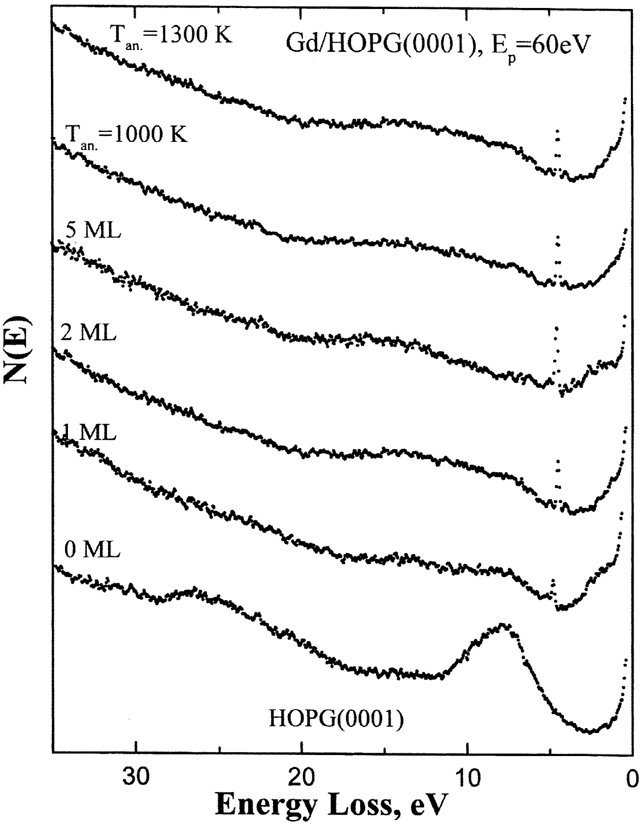

Fig. 3. Electron energy loss spectra taken with 60 eV incident electron beam energy for different Gd coverages deposited at 20 K and annealing temperatures of the Gd/HOPG interface at thick coverages ($\theta = 40$ Å).

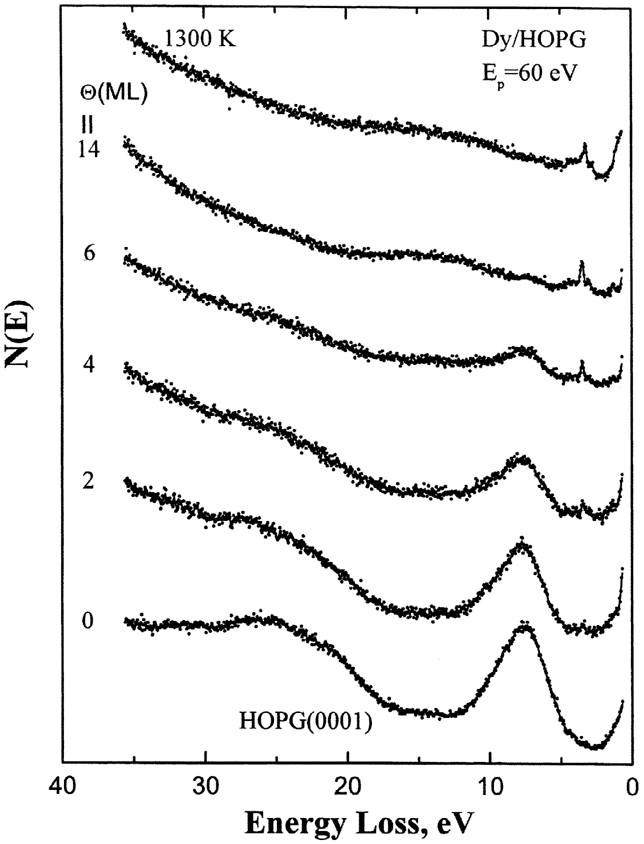

Fig. 4. Electron energy loss spectra ($E_p = 60$ eV) recorded for the Dy/HOPG interface at 20 K and after annealing of the system at 45 Å coverage.

In contrast to the spectra taken at 60 eV incident electron beam energy, the shape of the EELS spectra at high E_p changes remarkably after annealing at 1000 K and 1300 K. The intensity of the *5p–5d* excitation peaks increases and broad features at 15 eV and 3.5 eV appear. Similar losses were observed both for carbide-like systems of *d*-metals [14] and graphite intercalated compounds [15–17].

UPS studies also demonstrate formation of carbide-like systems after annealing of the Gd and Dy/HOPG interfaces at temperatures up to 1300 K. As an example, UPS spectra of the Gd/HOPG system are shown in Fig. 6. In the UPS spectrum of the clean HOPG(0001) the main feature originating from *p*-states of graphite is located at about 5.5 eV binding energy. During deposition of Gd, these *p*-states slightly shift (by 0.3 eV) to higher binding energies and peaks of the Gd *4f*- and *5d*-states start to

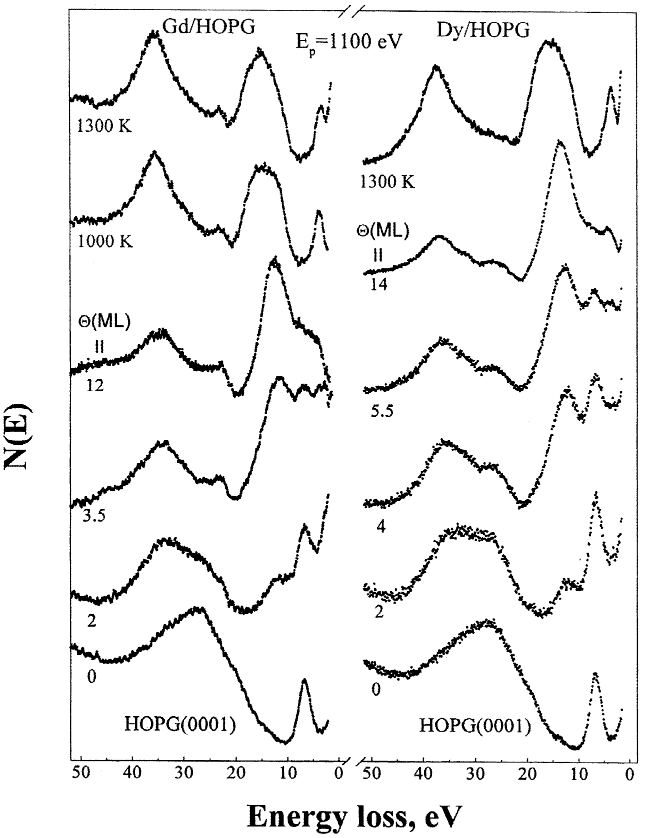

Fig. 5. Electron energy loss spectra taken with 1100 eV incident electron beam energy for various Gd and Dy coverages and annealing temperatures. The spectra were recorded at 300 K, Gd and Dy/HOPG systems were annealed at 40 and 45 Å coverages, respectively.

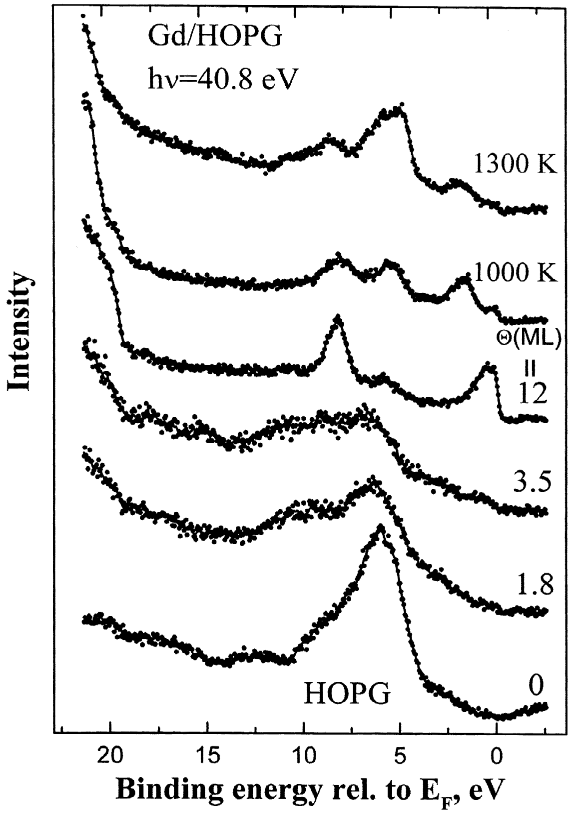

Fig. 6. Angle-integrated ultra-violet photoemission spectra of the Gd/HOPG system taken with He II (40.8 eV) radiation at 20 K as a function of Gd coverage and annealing temperature. The interface annealing was performed at 40 Å coverage.

grow at about 9 eV and near the Fermi level, respectively. The UPS spectrum taken after deposition of 12 ML of Gd exhibits a structure with features corresponding to the Gd *4f* (8.5 eV) and *5d* (near E_F)-states that is typical of metallic Gd.

After annealing of the Gd-HOPG interface at 1000 K, the intensities of the Gd *4f* and *5d* signals decrease whereas the peak of graphite *p*-states increases and shifts to lower binding energies relative to pristine HOPG. Besides, a new feature at about 2 eV appears. After annealing at 1300 K, the peaks corresponding to *p*-states of graphite and *4f*-states of Gd move further to lower and higher binding energies, respectively, while the density of states at the Fermi level (Gd *5d*-states) decreases. The observed shifts of the Gd and graphite features in opposite directions may be explained by the charge transfer from Gd *5d* to graphite $p_{\pi*}$-states that correlates with reduction of the *5d* feature in the UPS spectra. The obtained structure and evolution of photoemission spectra of the Gd/HOPG interface are close to the results reported for the La/HOPG system [2] and similar to photoemission spectra for carbides of *d*-metals [18,19].

According to our XPS data, binding energy of the C(1s) peak is almost insensitive to the increase in Gd and Dy coverage on HOPG and annealing of the interfaces at temperatures up to 1300 K. Shifts of the C(1s) peak during the experiments did not exceed 0.2 eV.

4. Conclusions

In summary, formation of the Gd and Dy/HOPG(0001) interfaces at 20 K and 300 K has been investigated by electron spectroscopies and LEED. The behavior of the interfaces upon Gd and Dy deposition was almost independent of the substrate temperature. For both interfaces we observed deviations from a monotonous decay in the attenuation curves for C(272) AES signal most clearly pronounced at coverages close to 1, 2, and 3 ML which may be related to diffusion of Gd and Dy atoms into interplane space of graphite.

LEED measurements showed different atomic structures for the Gd/HOPG and Dy/HOPG systems. A LEED image typical of clean HOPG(0001) was observed during Gd deposition up to 20 Å coverage and after annealing of the Gd/HOPG system at high coverages in the temperature range of 900–1300 K. For the Dy/HOPG interface at high coverages (20–45 Å) LEED pattern typical of clean HOPG(0001) coexisted with superstructural rings. The superstructure of $\sqrt{3}\times\sqrt{3}$ type was also monitored by LEED after annealing of the Dy/HOPG system at 600–1300 K.

According to UPS, AES, and LEED data, annealing of the interfaces at temperatures up to 1300 K induces, most probably, formation of the ordered carbide-like systems and higher temperatures are required to obtain Gd- and Dy-intercalated graphite.

Acknowledgements

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