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1999 J. Phys.: Condens. Matter 11 8453

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Synthesis of a weakly bonded graphite monolayer on Ni(111) by intercalation of silver

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Received 18 June 1999, in final form 17 August 1999

Abstract. Silver has been successfully intercalated underneath a monolayer of graphite (MG) adsorbed on Ni(111) by deposition on the MG/Ni(111) surface at room temperature and subsequent annealing to 350–400 °C. The surface phonon dispersion of the MG/Ag/Ni(111) system has been measured in the $\bar{\Gamma}\bar{K}$ direction of the Brillouin zone using high resolution electron energy loss spectroscopy. The dispersion curves were found to be almost identical to those of bulk graphite, which is in contrast to the softened graphite-like phonon modes observed for the MG/Ni(111) system. This suggests that the stiffening of the phonon modes induced by silver intercalation is caused by a weaker interaction of the π states of graphite with the substrate. These results demonstrate that a weakly bonded graphite monolayer, whose chemical properties are very similar to those of bulk graphite and which is stable up to 400 °C, can be synthesized *in situ* on Ni(111) after intercalation of silver.

1. Introduction

Recently a series of works devoted to investigation of the electronic and geometrical structure of thin film intercalation compounds appeared in the literature [1–5]. Such systems, formed by intercalation of monolayers of different metals underneath a monolayer of graphite (MG) on top of Ni(111) [1–3] and Ir(111) [4, 5], are interesting for several reasons. On the one hand, they exhibit an electronic structure and physical properties analogous to bulk classical graphite intercalation compounds (GICs) [6, 7]. On the other hand, they are low-dimensional systems which are expected to have quantum-size properties, such as oscillations of the valence band electron density near the Fermi level in dependence on the thickness of the intercalated metals, similar to those observed for the Ag/HOPG (highly oriented pyrolytic graphite) system [8]. On Ni(111), in particular, a well ordered commensurate MG(1 × 1) structure can be prepared as a consequence of the close fit between both lattice constants [1].

An additional advantage of this method of preparing intercalation-like compounds is the possibility of forming structures which cannot be created in bulk graphite, for example GIC-like structures based on the noble metals Cu, Ag and Au. We have recently shown that it is possible to intercalate a Cu layer underneath a monolayer of graphite adsorbed on Ni(111) [2]. The intercalated Cu monolayer causes a weakening of the MG–substrate interaction, as revealed by the corresponding surface phonon dispersion relations which were found to be very similar to those of bulk graphite, except for the observed stiffening of the longitudinal

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acoustical mode LA and the splitting of the LA and LO (longitudinal optical) modes at the $\bar{\Gamma}$ point of the BZ.

The possibility of preparing *in situ* a more perfect monolayer of graphite can be considered as the main motivation of our current work. We will demonstrate that our method consisting of depositing a thin Ag film onto the MG/Ni(111) system at room temperature followed by annealing to 350–400 °C allows us to intercalate Ag underneath the MG. This is in contrast with reported attempts to intercalate Ag underneath MG adsorbed on Ir(111) foils [4], which showed that direct intercalation of Ag into this system is impossible. Our investigation of the surface phonon dispersion of the MG/Ag/Ni(111) system by means of high-resolution electron energy loss spectroscopy (HREELS) shows that intercalation of Ag induces a stiffening of all graphite-derived phonon branches up to the energies characteristic for bulk graphite, independently of the thickness of initially deposited Ag overlayers. Here we present the phonon dispersion curves over the whole energy range in the $\bar{\Gamma}\bar{K}$ direction of the Brillouin zone.

2. Experiment

The experiments were conducted in a UHV system equipped with an ELS22 HREEL spectrometer consisting of two double cylindrical 127° deflectors, a LEED system and an ion gun. The base pressure in the experimental chamber was 5×10^{-11} mbar. The resolution of the HREEL spectrometer was about 8 meV with count rates of the specular reflected elastic beam of 10^{-5} – 10^{-6} cps at a primary electron energy of 19.1 eV. The primary energy has been set to this value in order to provide a parallel momentum transfer high enough to reach the BZ boundary. The measurements were performed at angles of incidence θ_i of 60 and 75° as measured from the surface normal. The off-specular angle θ_d was varied within the incidence plane between 75 and 15° during the measurement of the surface phonon dispersion. The Ni(111) crystal was mounted such that the sagittal plane coincided with the $\bar{\Gamma}\bar{K}$ direction of the Brillouin zone of the MG/Ni(111) surface.

The MG/Ag/Ni(111) system was prepared in two stages, following the method previously applied to prepare the MG/Cu/Ni(111) system [2]. Firstly, a monolayer of graphite was formed on top of Ni(111) by cracking of propylene (C_3H_6) at a sample temperature of 500 °C. The Ni(111) surface was found to saturate after exposure to a pressure of 1×10^{-6} mbar for 4 min. The corresponding LEED pattern displayed a sharp hexagonal structure characteristic of monocrystalline graphite. After that, about five to 12 monolayers of Ag were deposited onto the MG/Ni(111) surface at room temperature and then were annealed to 350–400 °C. This led to intercalation of Ag underneath the graphite monolayer, as demonstrated by the intensity increase of the reflected electron beam and the appearance of phonon dispersion curves. This was accompanied by formation of a weak additional (8×8) LEED superstructure with intensive little hexagons around each graphite-derived spot (not shown).

3. Results

Figure 1 shows typical HREEL spectra for the MG/Ag/Ni(111) system measured at different scattering angles, i.e. for different values of parallel momentum transfer Q_{\parallel} . The corresponding phonon dispersion curves along the $\bar{\Gamma}\bar{K}$ direction of the Brillouin zone are compared in figure 2 with the surface phonon dispersion of bulk graphite (from [10], dashed lines) and of the MG/Ni(111) system (from [2], dotted lines). A simple analysis of these data reveals that both systems are characterized by the same surface phonon modes characteristic of bulk graphite [2, 10]. We follow the notation introduced by Aizawa *et al* [11], in which the polarization

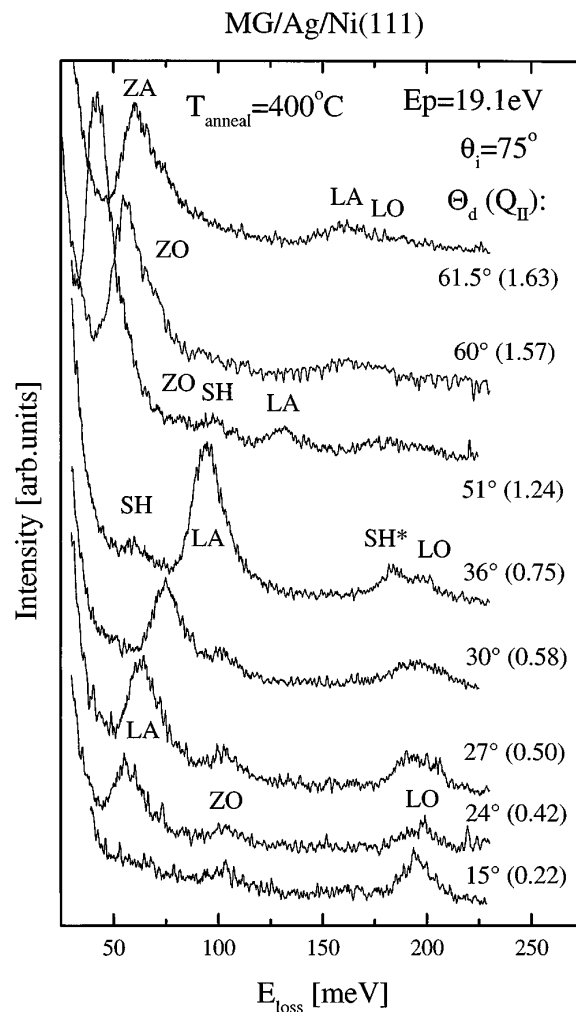


Figure 1. Series of HREEL spectra for the MG/Ag/Ni(111) system along the $\bar{\Gamma}\bar{K}$ direction of the Brillouin zone recorded at different scattering angles θ_i . The corresponding parallel momentum transfer Q_{\parallel} (in \AA^{-1}) is given in brackets. The different modes are the vertical acoustical mode ZA, the longitudinal acoustical mode LA, the acoustical shear horizontal mode SH, the vertical optical mode ZO, the optical shear horizontal mode SH* and the longitudinal optical mode LO.

of the different phonon modes is derived from a comparison with calculations. According to this, the branch labelled ZA in figure 2 is an acoustic-like mode in which two carbon atoms in the unit cell vibrate in phase and perpendicularly to the surface, and the ZO branch is a vertically vibrating optical mode. The LA and LO branches are a longitudinal acoustic mode and a longitudinal optical mode, respectively, and are associated with vibrations of carbon atoms parallel to the surface (i.e. in the direction of the σ bonds [9]). Since these modes do not differ so much from the bulk graphite ones, we can characterize these layers as graphite overlayers. The optical shear horizontal mode SH* is also observed, whereas the corresponding acoustical shear horizontal mode SH is not detected due to the scattering geometry used in experiment (see below). However, in comparison with the phonon modes of MG/Ni(111), the

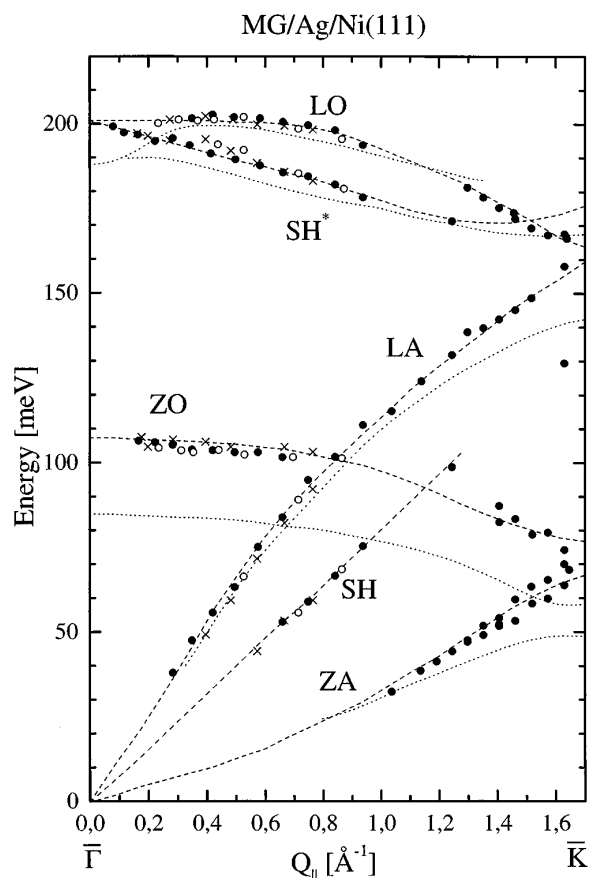


Figure 2. Surface phonon dispersion curves along the $\bar{\Gamma}\bar{K}$ direction of the Brillouin zone for the MG/Ag/Ni(111) system. The different graphite-derived modes are marked as ZA, LA, SH, ZO, SH* and LO. Data corresponding to bulk graphite and to the MG/Ni(111) system are shown by dashed lines (from [10]) and dotted lines (from [2]), respectively. Different symbols correspond to different thickness of initially deposited Ag overlayers or to different angles of incidence θ_i : (○) 5–7 ML, $\theta_i = 60^\circ$; (×) 10–12 ML, $\theta_i = 60^\circ$; (●) 10–12 ML, $\theta_i = 75^\circ$.

modes in the MG/Ag/Ni(111) system (and especially the ZO mode, connected with vibrations of carbon atoms perpendicular to the surface) are noticeably shifted towards higher energies and practically coincide with the modes characteristic of bulk graphite. This remarkable experimental fact resembles in some aspects the stiffening of the graphite-derived phonon modes observed after intercalation of Cu in the MG/Ni(111) system [2], although much better results are obtained after Ag intercalation (see discussion below). In both systems, the observed stiffening of the graphite-derived phonon is caused by a weakening of the MG–substrate interaction induced by the intercalated Cu, Ag layers. This is supported by the following arguments.

According to the studies of Oshima and Nagashima [9], the interaction of MG with a Ni(111) substrate is caused by orbital mixing of the MG π states with the Ni d states. This interaction is covalent-like and leads to a significant softening of the graphite-derived phonon modes in comparison with those of bulk graphite. Noble metals (Ag, Cu) have a valence band structure with filled d orbitals, which are located at binding energies of 4 and 2 eV,

respectively. Therefore, the corresponding valence bands have an s-like structure. As a result, the interaction of MG with these metals has a different character. Moreover, differences in the values of the electronegativities between carbon and noble metals are significantly lower than those between carbon and alkali metals (also s metals). Therefore, the charge transfer and, consequently, the interaction between C and Ag is expected to be even weaker than those observed in alkali-metal-derived GICs [6, 7], possibly up to the level of interplanar interaction in bulk graphite. This is actually what we observe for the MG/Ag/Ni(111) system. The weakening of the MG–Ag bonding leads to an orientation misfit between the MG and the underlying Ag layer, which is responsible for the appearance of the SH mode in the phonon dispersion (note that symmetry considerations rule out a coupling of electrons to the SH mode in sagittal plane scattering [12]).

Now we turn to the question of the amount of Ag intercalated underneath the monolayer of graphite. As shown by the data in figure 2, almost identical phonon dispersion curves were measured after depositing 5–7 ML Ag (open circles) or 10–12 ML Ag (other points), suggesting that the deposited Ag layers have been intercalated when preparing the MG/Ag/Ni(111) system. We mention for comparison that recent PES and STM investigation of the MG/Cu/Ni(111) system [13] shows that all the deposited Cu overlayers are intercalated underneath MG. It was noted in [4] that the maximal amount of Ag which can be intercalated in the MG/Ir(111) foil system by way of substitution of alkali metals is only one monolayer, leaving Ag atom islands on top of the substrate. In the case of the MG/Ag/Ni(111) system, we cannot determine the amount of Ag intercalated underneath MG on Ni(111). However, on the basis of the high sensitivity of HREELS to residual gases we can conclude that just a very small part of the surface could still be covered by Ag, since some additional, low intensity peaks could be detected at $\theta_d = 0^\circ$ only when the surface was kept for a long time (\sim two hours) at room temperature without flash annealing. On the other hand, and since tails of the phonon branches characteristic of the MG/Ni(111) system are not observed after Ag intercalation, we can conclude that most of the deposited Ag layers are intercalated underneath MG.

We would like to point out that in spite of having very similar phonon dispersion curves, the two systems MG/Ag/Ni(111) and MG/Cu/Ni(111) exhibit some significant differences. Whereas in the case of the MG/Ag/Ni(111) system the phonon spectra have practically the same structure as for bulk graphite, for the MG/Cu/Ni(111) system an additional stiffening of the LA mode as compared to graphite is observed (which suggests a strengthening of the σ bonds after Cu intercalation) as well as some softening of the LO and ZO modes near the $\bar{\Gamma}$ point of the BZ.

In summary, we have successfully intercalated Ag underneath a monolayer of graphite adsorbed on Ni(111) by deposition onto the MG/Ni(111) surface at room temperature with subsequent annealing to 350–400 °C. The surface phonon dispersion of the MG/Ag/Ni(111) system has been measured in the $\bar{\Gamma}\bar{K}$ direction of the Brillouin zone by means of HREELS. They were found to be almost identical to those of bulk graphite, independently of the thickness of the initially deposited Ag overlayers in the range of 5 to 12 ML. These results demonstrate that a weakly bonded, well ordered and stable up to 400 °C graphite monolayer can be synthesized *in situ* on Ni(111) by means of silver intercalation.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft, by the programmes ‘Surface atomic structures’ and ‘Fullerenes and atomic clusters’ and by the RFFI–DFG Programme (project 98-03-04071). AMSh is grateful to Freie Universität Berlin for financial support and hospitality. The authors wish to thank Ch Roth for technical assistance.

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