Transition Metals on the (0001) Surface of Graphite: Fundamental Aspects of Adsorption, Diffusion, and Morphology

by

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Abstract.

In this article, we review basic information about the interaction of transition metal atoms with the (0001) surface of graphite, especially fundamental phenomena related to growth. Those phenomena involve adatom-surface bonding, diffusion, morphology of metal clusters, interactions with steps and sputter-induced defects, condensation, and desorption. General traits emerge which have not been summarized previously. Some of these features are rather surprising when compared with metal-on-metal adsorption and growth. Opportunities for future work are pointed out.

1. Introduction.

Graphite is an intriguing support for metals because of its inertness in aggressive environments, as well as its low cost and high abundance. A major application for graphite-supported metals is lithium ion batteries [1, 2]. In fact, the demand for these batteries is expanding so quickly that it currently drives the international market in graphite [1]. An important application on the horizon is biofuel conversion, where graphite (or other carbon-based materials) may provide robust supports for catalysts in aqueous media [3].

Adsorption of transition metals and noble metals on graphite has been studied for many years—starting well before the discovery of graphene, carbon nanotubes, or even C₆₀. Actually, adsorption of metals on graphite provides a benchmark and point of entry for understanding metal interaction with these more-recently discovered forms of carbon. Even more broadly, graphite has been regarded as a good substrate for model investigations of surface phenomena, e.g. catalysis by supported metal particles [4].

Among the metals, alkali metals have received special attention because of their role in batteries, and they have been reviewed thoroughly by Caragiu and Finberg [5]. In this article, we focus on the transition metals including the coinage metals, i.e. metals in groups 3-11, and we exclude the rare earths. ("Metal" henceforth designates this defined set.) We review the literature in addition to providing some new data. We do not attempt to provide a comprehensive overview of the literature (much of which is rather

phenomenological), but rather we focus on the *fundamental aspects* of the interaction of metal atoms with a graphite surface. These fundamental aspects include: (1) strength of the metal-carbon adsorption bond; (2) diffusion coefficient; (3) adsorption and desorption kinetics; (4) long-range electronic response of the substrate; (5) shapes of atomic aggregates; and (6) the influence of defects.

It will also be informative to compare some of these aspects of metals on *graphite* with those of metals on *metals*. For the latter, a broad understanding of mechanisms, kinetics, and thermodynamics of deposition, nucleation, and growth has been established [6-9]. To some extent, this conceptual framework is very useful and it can be applied to metals on graphite, but we will show that there are also significant differences. One example is the condensation coefficient as defined in Section 9. For a metal atom on a *metal* surface, at room temperature (nominally 300 K), this quantity can be safely assumed to be unity. For a metal atom on a *graphite* surface, there is considerable evidence that this quantity is less than unity. Another example is the diffusion barrier of a single atom. For metals on metals, diffusion barriers are typically a few tenths of eV, whereas for the same metals on graphite, diffusion barriers can be lower by an order of magnitude. Differences, such as these in condensation coefficient and diffusion barrier, can require widely different interpretive frameworks for experimental data in the two types of systems.

In this article, we focus on metals deposited via physical vapor deposition, because this technique is most favorable for understanding metal deposition in terms of a sequence of simple atomic processes, beginning with *impingement of single atoms* at the surface. The subsequent sequence can then include diffusion of atoms, nucleation and growth of clusters, desorption, and/or interaction with step edges. There exists a considerable body of complementary work in which *pre-formed metal clusters* are deposited onto the graphite surface. Because that approach can provide a high level of control and surface homogeneity, it holds considerable promise for nanotechnology, but it is not emphasized here. Aspects of that body of work have been summarized elsewhere [10-12].

2. Overview of the experimental context.

Metals can be deposited on graphite using a wide variety of techniques, ranging from wet (chemical) methods to gas-phase methods [11, 13-16]. As mentioned in the Introduction, this article focuses on the method of physical vapor deposition, because in that process, single atoms impinge on the graphite surface, leading most directly to atomic-scale insights.

Before the early to mid-1990s, it was common for the metal to be evaporated in a vacuum chamber normally dedicated to coating samples in preparation for electron microscopy. In these coaters, the base pressure was as high as 10^{-5} mbarr. The sample was then transferred in air to an electron or optical microscope, or (starting in 1986) it could be analyzed via scanning probe microscopies [17-21]. The environments of air, and of low to high vacuum—rather than continuous ultrahigh vacuum (UHV)—were assumed to be acceptable because of the inertness of graphite. It is true that, even in air, graphite surfaces can often be imaged as smooth terraces that are on the order of a micron wide. On these terraces, atomic-scale images that reflect the honeycomb carbon structure

(shown in Fig. 1) are commonly reported, especially using STM [17-21]. Examples of micron-wide terraces, and atomic-scale resolution are shown in Fig. 2(a-b). In fact, because of HOPG's atomic-scale perfection in air, undergraduate laboratory experiments have been designed to image graphite or modified graphite surfaces with scanning probe microscopies, e.g. [22-24].

However, graphite is not completely inert. In a study of Au deposition in the 1960s, it was already reported that exposure to water or cleaning solvents had a strong effect on the density of Au clusters on graphite, based on electron microscopy [25]. In the 1970s, it was found that Au nucleation and growth is significantly different on graphite that has been cleaved in UHV, than on graphite cleaved and allowed to rest in air for several hours [26]. In fact, the density of Au nuclei depends systematically upon the time that a cleaved graphite surface spends in air before Au is deposited upon it [27]. These observations are probably explained by the adsorption of hydrocarbons, which causes the surface properties of graphene and graphite to change during exposure to air (over a few tens of minutes) [28]. Presumably, the hydrocarbons are too mobile to be imaged effectively with scanning probe techniques, at least at the typical observation temperature of 300 K, so the surface may appear deceptively clean when analyzed with such techniques.

Independent of the environment's effect on the graphite substrate, environment may affect the chemical state of the metal or the distribution of metal on the surface during or after deposition, especially via oxidation or via enhancement of restructuring rates [29]. Recently, for instance, it has been reported that exposure to CO(g) accelerates coarsening of Pd nanoclusters on a graphene surface [30]. In short, there are many reasons to be skeptical about the total inertness of metal-on-graphite systems, and to value UHV as a component of these experimental studies.

There are various grades and sources of graphite. Highly-oriented pyrolytic graphite (HOPG) is a synthetic form available in large samples with high purity and high structural perfection. (A synthetic form of graphite known as Kish graphite, with lower purity and smaller sample size, can be considered the historical precursor of HOPG [31].) The highest-quality material is employed in X-ray and neutron optics, where the structural quality of HOPG is judged by its mosaic spread. Grades are usually designated ZYH, ZYB, and ZYA, with ZYA having the smallest mosaic spread ($0.4^\circ \pm 0.1^\circ$) and largest grain size (up to 3 mm) [31].

HOPG cleaves easily along the basal plane. A fresh surface is prepared by pressing on, then peeling off, a piece of tape. A thin sheet of HOPG (as thin as one atomic layer—graphene [32, 33]) clings to the tape and leaves a fresh graphite surface behind. Often, these graphite surfaces exhibit flat, micron-size terraces, but defects can be found. These defects fall into two classes: (1) long-range imperfections, including dislocations and associated stacking faults [25, 34-42], as well as folds of the top carbon sheet [39]; and (2) small localized defects which may be single-atom vacancies in the top carbon sheet, inclusions, or adsorbates [43-48]. For illustration, an extensively-folded region (type 1 defect) is illustrated in Fig. 2(c). An inclusion (type 2 defect)—with the HOPG lattice visible over the inclusion—is illustrated in Fig. 2(d). Defects of type 1 can be modified or even created under the influence of a scanning probe tip. Defects of type 2 occur at densities ranging from $1 \times 10^{-8} \text{ nm}^{-2}$ to $1 \times 10^{-4} \text{ nm}^{-2}$ [43-48], with no obvious

correlation to HOPG grade. The latter values correspond to 5×10^{-10} to 5×10^{-6} defects per C atom in the surface plane.

Even in the most careful studies, graphite is usually cleaved in air and then transferred to UHV, rather than being cleaved in situ. Following transfer, the surface is often heated before metal is deposited. The highest reported cleaning temperature, in UHV, is 2500 K [49, 50]. Metois, Heyraud and Takeda [27] have reviewed studies of various procedures for cleaning HOPG by thermal annealing. In our own work, we have experimented with thermal treatments in the range 300 K to 1300 K, and have found that heating ZYA or ZYH to 800 K for several tens of minutes in UHV is effective.

Because fundamental energetic and mechanistic information is our objective, this review relies most heavily on experimental studies from the recent literature where deposition and analysis were conducted entirely and continuously in UHV, although some papers from other types of experiments are also noted.

As a final comment, in our experience, metals on graphite surfaces are surprisingly difficult to work with, using scanning probe techniques. This is because the tip interacts strongly with the metal particles. The reason for this is discussed further in the following section. Consequently, tip stability and experimental reproducibility can be more challenging than in metal-on-metal experiments. Tip effects are illustrated in Fig. 3.

3. Bonding of a metal adatom to the basal plane.

Theory is the source of all information currently available about the adsorption energy (E_a) of metal atoms on graphite. However, two comments about the theoretical landscape are relevant. First, a number of papers nominally model metal adsorption on graphite, but they use a single sheet of sp^2 -hybridized carbon to model the carbon surface. Hence, they are more appropriately regarded as models of free-standing *graphene* than *graphite*. This is especially true of work that was conducted before the experimental characterization of graphene in 2004 [32, 33]. Table 1 summarizes values of adsorption energy for several metals. Only a small number of results are shown, because we apply a filter to the literature: models must incorporate two or more carbon sheets in order to be included in this Table.

Second, it is known that London dispersion forces are important in the bonding between graphite sheets. However, before the late 2000's, it was not common to include dispersion forces in DFT. Perhaps for this reason, some theoretical papers reported that a metal atom's adsorption energy was the same, regardless of whether one carbon sheet or multiple carbon sheets were used as the model of graphite [51, 52]. But the values for Cr and Au in Table 1, from the work of Hardcastle et al. [53], clearly show that the metal atom's adsorption energy increases significantly as the number of carbon sheets increases from 1 to 3 when dispersion forces are included. Hence, results for metals on (1-layer) graphene cannot be simply transposed to graphite. Instead, the adsorption energy for a metal on graphene sets the *lower limit* on the value for graphite.

Table 2 compares good values (selected in accord with the discussion above) for adsorption energies of metal adatoms at optimal sites on three substrates: single-layer graphene ($E_{a/graphene}$), graphite ($E_{a/graphite}$), and the densest low-index surface of the respective metal ($E_{a/metal}$). Note that, for the fcc or hcp metals, $E_{a/metal}$ is the binding energy of a single metal atom on the close-packed surface of the same metal, in the

natural three-fold hollow growth site. For the bcc metal Cr, $E_{a/\text{metal}}$ is the binding energy at the long-bridge site of the (110) surface, which is expected to be the preferred site.

Table 2 shows that a simple qualitative relationship holds true for the 5 metals:

$$E_{a/\text{graphene}} < E_{a/\text{graphite}} < E_{a/\text{metal}} \quad (1)$$

This relationship can probably be applied as a check on the reasonableness of measured or calculated values of $E_{a/\text{graphite}}$ for metals not included in the Table. To do this, of course, one needs access to reliable values for $E_{a/\text{graphene}}$ and $E_{a/\text{metal}}$. Values of $E_{a/\text{graphene}}$ are available elsewhere [54, 55]. With regard to $E_{a/\text{metal}}$, this is relatively simple to calculate but it has not been tabulated elsewhere and values are in fact difficult to find in the literature. Therefore, we have calculated several values and collected them in Table 3, as a convenient reference [56].

Because $E_{a/\text{graphene}}$ sets the lower limit in Eq. (1), we briefly review its trends among 3d metals [54, 55]. First consider the variation along a single row. For the first-row 3d-transition metals V through Ni, $E_{a/\text{graphene}}$ falls in the range 0.87-1.54 eV except for Cr and Mn. The values for the latter two metals define a deep minimum (corresponding to weak binding) at only 0.18 and 0.16 eV, respectively. Next consider the metals in a single column, group 10: Ni, Pd, Pt. For these metals, $E_{a/\text{graphene}}$ ranges from 1.08 to 1.55 eV, i.e. within the same range as most of the first-row transition metals. Finally, consider the coinage metals, group 11: Cu, Ag, and Au. Here, the interaction with graphene is very weak, only 0.02 to 0.23 eV. Based upon this information, the variation in absolute value across a row is greater than the variation within a column. Specifically, the variation across the first row is 1.38 eV, much greater than the variation in groups 10 and 11, which is only 0.47 and 0.21 eV respectively. Metals near half-filled d-shells (Cr, Mn) and formally filled d-shells (Cu, Ag, Au) have adsorption energies below 0.25 eV, and interact more weakly with graphene than do other metals. In fact, the metals with adsorption energies below about 0.5 eV can be described as *physisorbed*, while the others are *chemisorbed* [57]. Of course, calculations (and measurements!) for more transition metals on graphene will surely emerge to test and refine these generalizations.

For the chemisorbed metals, bonding with the graphene surface is covalent. The bonding-induced change in electron density is mainly localized on the carbon atoms closest to the metal adatom [54, 55]. Among the physisorbed metals, Au exhibits net electron transfer *from* the substrate *to* the metal adatom, in keeping with the fact that Au is a very electronegative metal [58, 59].

As stated in Eq. (1), bonding of metal adatoms with *graphite* is stronger than bonding with *graphene*, but to first order, one expects the trends in E_a noted above to be similar for *graphite*. The reason for the higher adsorption energies on *graphite* is undoubtedly related to the dispersion forces which bind the carbon sheets, as noted by Hardcastle et al.[53]. However, no detailed analysis is available (to our knowledge) and this topic is ripe for detailed analysis.

The classic means of *measuring* adsorption energies is temperature programmed desorption (TPD). However, this is not useful for metals on *graphite*, because the barrier for a single metal atom to desorb into the gas phase is controlled by its bonding to the metal cluster, not its bonding to *graphite*. Results from an elegant TPD study of Cu on

graphite by Arthur and Cho [49] are consistent with this feature. There, it was found that the desorption barrier of Cu on graphite converged to the enthalpy of vaporization of bulk Cu at a Cu coverage of about 3 layer-equivalents. Deviation to smaller desorption energies at lower Cu coverage was ascribed to the increasing deviation of smaller Cu clusters from bulk metal.

In another type of measurement, the contact angle between annealed, near-hemispherical Au clusters and the HOPG surface was measured using scanning electron microscopy [60, 61]. This yielded a value for the interaction energy of 0.26 eV per Au atom at the interface. However, one expects this value to be lower than the adsorption energy of a single Au adatom on HOPG. This expectation is consistent with the calculated values for $E_{a/\text{graphite}}$ of Au adatoms in Table 1, all of which are above 0.26 eV.

The basal plane of graphite is shown schematically in Fig. 1, with high-symmetry sites labeled. The possible high-symmetry adsorption sites on the basal plane of graphite are the same as on graphene—hollow (H), bridge (B), and top (T)—with one exception. On graphite there are two types of T sites, due to the ABAB stacking of the carbon sheets. In the T_α site, a carbon atom in the second layer sits directly beneath a carbon atom in the top layer, whereas in the T_β site, the second layer is empty. The best calculations available at present (Table 1) show that the favored site of a Cr adatom is H, of a Pt adatom is B (bridge, also called bond center), and the site of Ag, Au, and Cu adatoms is T_β . The prediction of the T_β site for Au is confirmed by experimental results [53, 62].

The relatively weak interaction between metals and graphite may be related to the common observation of time-dependent changes during STM imaging of these surfaces [62-67]. For example, Clark et al.[64] reported that a small 2D Pt cluster on graphite moved by tens of nm, relative to a defect site, from one image to the next. It is difficult to determine the extent to which such changes are tip-induced, or represent intrinsic dynamic phenomena at the surface. In either case, however, one expects motion and instability to be facilitated by the relatively low value of $E_{a/\text{graphite}}$.

The issue of intercalation of metals in graphite also relates to surface adsorption. It is known that adsorbed metals—not only transition metals, but also other types of metals—can be buried beneath sheets of supported *graphene*, e.g. [68-73]. It is also known that some *non-transition metals* can intercalate in graphite surfaces, e.g. [74, 75]. However, we know of no evidence for intercalation of *transition* metal atoms in *graphite* surfaces, at least under the conditions typical of surface science experiments. There is no obvious reason why intercalation of transition metals should not occur, at least at sufficiently high temperature and high metal supersaturation. However, this possibility has rarely (if ever) been entertained when interpreting surface data for adsorption of transition metals on graphite.

4. Surface diffusion.

To a good approximation, the diffusion barrier on graphite (and graphene) can be equated to the minimum *difference* in adsorption energies between the favored sites, and high-symmetry locations between favored sites along physically-accessible pathways. This value, ΔE , has been calculated for a few metals on graphite (Table 1). Comparing only values from Ref. [76], for the sake of self-consistency, the trends in $\Delta E_{\text{graphite}}$ parallel

those in $E_{a,\text{graphite}}$. For instance, $\Delta E_{\text{graphite}}$ is highest for the strongly-bonded metal Pt, and lowest for the weakly-bonded metal Ag.

Furthermore, the diffusion barrier for a metal on graphite consistently falls below the corresponding metal-on-metal diffusion barrier, but it can be either higher or lower than its diffusion barrier on graphene. For example, for the strongly-bound metal Pt, $\Delta E_{\text{graphite}} = 0.16$ eV (Table 1), which is lower than the value $\Delta E_{\text{graphene}} = 0.19$ eV [54]. By contrast, for Cu, $\Delta E_{\text{graphite}} = 0.02$ eV (Table 1), which is much higher than the value $\Delta E_{\text{graphene}} = 0.004$ eV [54]. These trends can be summarized as: $\Delta E_{\text{graphene}} \lesseqgtr \Delta E_{\text{graphite}} < \Delta E_{\text{metal}}$.

There are some experimentally-derived values for the diffusion barrier of metals on HOPG, but these are rather inconsistent. Ganz et al. reported $\Delta E > 0.65$ eV for isolated Ag adatoms and $\Delta E > 0.8$ eV for isolated Au on HOPG. This was derived from the lifetimes of a few species thought to be isolated metal atoms, using STM [62]. However, this is unreasonable, since then for these systems $\Delta E \gg E_{a/\text{graphite}}$ where $E_{a/\text{graphite}} = 0.28$ eV for Ag and $E_{a/\text{graphite}} = 0.50$ eV for Au according to Table 1. Furthermore, Anton et al. estimated the *difference* $E_{a/\text{graphite}} - \Delta E = 0.40$ eV for Au on HOPG [77-79]. To achieve this, they derived the mean diffusion length of an Au atom (before desorption), from densities of metal islands imaged with TEM. Invoking the data of Arthur and Cho [49] to estimate an upper limit of $E_{a/\text{graphite}}$, Anton et al. could then set a limit of $\Delta E < 0.24$ eV for Au [77]. This limit is consistent with all of the calculated values shown in Table 1, but it is not consistent with the work of Ganz et al. [62]. Thus, it is doubtful that the rather high estimates of diffusion barrier for Ag adatoms ($\Delta E > 0.65$ eV) and Au adatoms ($\Delta E > 0.8$ eV) [62] are correct..

Diffusion of metal clusters, rather than single metal atoms, is also possible. On some metal surfaces, diffusion of small metal clusters containing several metal atoms is known [9, 80], and is sure to be facilitated even further by the relatively weak binding between metals and graphite. In two interesting studies, large, spherical, size-selected clusters of Au and Pt—containing hundreds or even thousands of atoms—were deposited on graphite. These large clusters were observed to diffuse and (at least for Au) coalesce at 300 K [81, 82]. Diffusion of smaller clusters that form by aggregation of individual atoms on the surface may be similarly feasible, provided that the cluster shape is reasonably compact.

5. Morphology of metal clusters on graphite.

Kern et al. have derived an approximate energetic criterion by which 2D vs. 3D growth can be predicted under conditions of thermodynamic equilibrium [8]. In terms of the variables we have defined, the condition for 3D growth is

$$E_{a/\text{graphite}} < E_{a/\text{metal}} \quad (2)$$

(and the inverse is true for 2D growth). It is clear from the discussion in Section 3 [cf. Eq. (1)], and the data in Table 2, that the condition for 3D growth is met easily for Cr, Pt, Cu, Au, and Ag, and one can reasonably expect this condition to be met for most, if not all, other metals. The expectation of 3D growth is thus based on the relatively weak metal-graphite bond introduced in Section 3.

In general, metals on graphite do exhibit compact 3D growth. Examples of compact 3D clusters are shown in Fig. 4(a-d) [63, 77, 83-85]. (Note that these islands all exist on the terraces of the basal plane.) Sometimes the clusters have discernible facets, although often the facets are only visible after annealing above 300 K. Heating also induces island coarsening, and the consequent increase in the average size makes facets easier to resolve.

There are at least two notable exceptions to the phenomenon of compact 3D growth.

First, Au [26, 27, 77, 86-93] and Pt [85] form dendritic multilayer islands around 300 K, as shown in Fig. 4(e-f). (Similar dendritic growth has been observed for the rare earth metal Eu on graphene at 300 K [55, 94, 95].) Dendritic-type shapes are also well known in metal-on-metal growth systems [96-98]. This growth shape is a signature of diffusion-limited aggregation, in which particles attach at edges of islands but have limited mobility along the edges after attachment. Fractal or fractal-like islands of Au and Pt on graphite are more than a single atom thick (hence 3D-like) but are rather flat (hence 2D-like). For instance, Au dendrites are 1 to 2 nm tall (roughly 4-8 atomic layers high), in the low coverage regime where they are separated laterally [77, 87]. This indicates that upward diffusion of Au and Pt atoms becomes improbable beyond a certain thickness. The fact that the dendritic shape is kinetically limited is consistent with the existence of compact 3D crystallites after growth at, or annealing to, elevated temperature [78, 86, 88, 92, 93]. Note that most studies of dendritic growth have involved some exposure to non-UHV environments, but dendritic growth is not due to contamination [26].

The second exception is this. Several authors have reported that 3D growth of large clusters, like those shown in Fig. 4, is preceded by the establishment of much smaller 2D islands. This has been reported for Mo [65], Pt [64, 99], Ag [62, 67, 100], Cu [62], and Au [62, 67]. Examples are shown in Fig. 5. Some authors report that these small 2D islands are less susceptible to change during STM scanning, than their larger 3D counterparts [65, 100]. Atomic-scale images indicate a variety of arrangements of metal atoms in these small islands, even within a single investigation [62, 64, 67]. Therefore, it is conceivable that defects or impurities play a role in stabilizing small 2D islands, and this may warrant further clarification.

6. Charge density modulations.

Metal atoms and clusters on graphite induce charge density modulations (CDMs) in the carbon support [101]. CDMs have been reported in STM studies of Ag [100], Mo [65], and Pt [99] on graphite. A signature of the CDM is an apparent $(\sqrt{3} \times \sqrt{3})R30^\circ$ periodicity in the carbon lattice, extending a few nm out from the metal [65, 99-101]. CDMs are not observed universally, however. For instance, CDMs were observed in one STM study of Ag on graphite [100] but not in another [62].

In metal-on-metal epitaxy, it is known that CDMs in the metal surface can lead to long- and intermediate-range electronic interactions between metal adsorbates [102, 103]. This in turn can influence nucleation and growth of metal islands [102]. Hence, it is not unreasonable to expect that CDMs may influence metal nucleation and growth on graphite, although that topic has not been explored to our knowledge.

7. Step edge decoration.

In addition to forming clusters and islands on the terraces, metals decorate step edges on graphite surfaces [47, 63, 100, 104-107]. This has been shown for many metals under many different conditions. Examples are shown in Fig. 6. Step decoration is also clearly visible in Fig. 4(a) and (e). The steps thus serve as potential templates for one-dimensional nanowires, though individual clusters at steps do not usually merge into uniform, single crystalline nanowires.

Step decoration reflects low binding energy and fast diffusion for metal atoms or small metal clusters on terraces of the basal plane, as discussed above. Consistent with this, calculations show that the binding energy of a metal adatom is higher at the edge of a graphene sheet—which can be taken as a model of a graphite step—than on the 2D part of (1 to 3-layer) graphene [53]. This can be ascribed to the dangling bonds present at the edge of the sheet.

But other adsorbates should also bond more strongly at step edges. Our own work, exemplified in Fig. 7, shows that there is significant variation among step edge shapes on nominally-clean graphite. Fig. 7(a) shows the most common case: The step edge has a square-step-profile, as expected for a clean step, in some regions. In other places the same step shows an upward bump in its profile, which is likely a contaminant. (Note that metals also produce this upward bump.) We thus believe that there is heterogeneity in the cleanliness of step edges on "clean" graphite. Perhaps the binding energies of metals at graphite steps are sufficiently high that they displace typical contaminants, leading to the consistent observations of metal step decoration noted above.

Typically, metal-decorated step edges co-exist with metal clusters on the terraces. However, it has been shown that some conditions of growth yield step decoration exclusively, at least at low metal coverage (a few monolayers or less). One such technique is deposition at—or annealing to—elevated temperature, as demonstrated with Au [88, 100], and with Fe [83]. This can be viewed as a manifestation of coarsening, and is not unexpected. Another technique leading to pure step decoration is growth from an organometallic precursor, demonstrated with Pt [16].

There have been two reports that HOPG steps of different heights are decorated differently, though both involved sample transfers in air [25, 100]. In the first, Hennig reported SEM data showing that "the capacity for a [HOPG] step to capture an adatom [of Ag or Au], i.e. to act as a perfect adatom 'sink' and then nucleate a cluster, seems to increase with step height." He concluded that heights below 3 atomic layers were inactive [25]. Later, Francis et al. reached the same conclusion based upon STM work with the same systems [100]. In spite of many experimental observations of step decoration, these are the only two reports of a dependence on step height in the literature.

Our own work indicates that the reported height-dependence of metal attachment may be spurious. Fig. 8 shows steps on graphite that are 1-, 2-, 3-, and 5-layers high, following physical vapor deposition of Cu. Steps are preferentially decorated in all cases, with the Cu clusters significantly higher than the adjoining graphite terraces. Each image was taken in a separate experiment. There is no evidence that smaller steps are more inert. Any difference in the probability for metal capture at different steps is more likely to be due to the degree of pre-decoration (contamination), illustrated in Fig. 7.

An interesting variant of step decoration involves circular step edges, which can be formed by oxidizing graphite at elevated temperature [25, 47, 104-106, 108]. Oxidation etches away the graphite, starting at pre-existing defects and moving outward in a circle. This forms circular, flat-bottom pits, sometimes called "vacancy loops"[25] or "molecule corrals." [47] The circular step edges of these pits can then be decorated with metals, as first demonstrated by Hennig [25]. An example of Hennig's early work is shown in Fig. 9(a) [25], and an example of more recent work from McBride et al. [47] in Fig. 9(b). The morphology that can be created in this way is quite striking.

8. Role of terrace defects.

In order to clarify the role of localized terrace defects in metal growth—especially carbon atom vacancies—several groups have created artificial defects via ion sputtering, and have studied metal deposition on these surfaces [63, 83, 85, 109]. Examples of STM images of grown metals are shown in Fig. 11. Comparison with the more perfect surfaces shows that, on the sputtered surfaces, metal clusters are more rounded, have a narrower size distribution, and are much more numerous. This is consistently attributed to preferential nucleation and pinning at the sputter-induced defect sites. The metal coverage is also higher on the sputtered surfaces, which is attributed to an increased condensation coefficient (vide infra). Interestingly, the metal clusters on sputtered graphite are easier to image with STM than on pristine graphite, suggesting that defect sites stabilize the metal clusters against tip interactions.

Considerable work has been done to investigate deposition of *pre-formed metal clusters* on graphite substrates that had been deliberately damaged or patterned with an ion beam, e.g. [110-112]. This approach is quite promising for developing ordered arrays of pinned metal nanoparticles, including nanoparticles of magnetic alloys [110]. It has even been shown that the metal clusters themselves can be deposited with sufficient kinetic energy to create defects in the carbon surface upon impact [11, 113].

9. Condensation and desorption.

In this section we will focus on the condensation coefficient, σ . We define this, after Venables [114], as the total amount of metal on the graphite surface divided by the total (time-integrated) metal flux. This is the quantity which is most easily measured and most important in a practical sense, although its derivative, σ' , has greater physical significance. The latter quantity, σ' , is the instantaneous condensation coefficient, i.e. the instantaneous change in adsorbate population per unit flux. Both quantities reflect the efficiency with which atoms accrue on a surface, as opposed to being reflected, or trapped and then desorbed, into the gas phase. (We take care to define these terms because condensation coefficient and its derivative belong to a group of closely-related terms, including sticking coefficient and accommodation coefficient, whose usage varies slightly among different communities, e.g. [57, 114-116].)

A number of authors have observed that at 300 K, σ is less than unity for metal atoms on graphite [49, 63, 77, 85]. Usually, this conclusion is based on evaluating the amount of metal on the surface in relation to the total flux that impinged on the surface. For instance, Lopez-Salido et al. [63], using both STM and XPS, found that the amount of Ag deposited on a pristine HOPG surface was only 0.1 times that on a heavily sputtered surface. Howells et al. [85] concluded that $\sigma < 0.1$ for Pt on graphite, by

measuring the Pt coverage on graphite vs. its coverage on a Ta plate close to the sample, with XPS.

In a different approach, Arthur and Cho [49] employed the method of King and Wells [117] to obtain σ' . With this method, the intensity of a scattered beam is measured with a mass spectrometer as a function of time, after a shutter is opened to allow impingement of an incident gas beam on the sample. For Cu and Au on graphite, Arthur and Cho observed that the scattered beam intensity is initially high and decreases steadily with time, as illustrated in Fig. 10. This corresponds to an initially low value of σ' that increases with time (with metal coverage). They interpreted this to mean that a metal atom has only a short lifetime on graphite before it desorbs again into the gas phase. As metal clusters nucleate, incoming metal atoms become increasingly likely to find their way into existing metal clusters, from which desorption is essentially impossible at 300 K. Arthur and Cho found that for both Cu and Au, $\sigma' = 0.05$ initially, and σ' approaches 1 at high metal coverage. The adsorption data were fit well with a kinetic model in which the growing clusters are 2D rather than 3D. This is consistent with the (puzzling) observations of small 2D islands noted above.

The observation of σ (or $\sigma') < 1$ may be surprising to scientists who work with metals on other types of solid surfaces (metals, oxides, semiconductors), where condensation coefficients are (reasonably) assumed to be unity at ambient temperature. For some metals, the different behavior on graphite may be attributable to low adsorption energy. For instance, at 300 K, the desorption rate for a coinage metal adatom on graphite is appreciable. For Au, $E_{a,\text{graphite}} = 0.56$ eV (cf. Table 1). If the pre-exponential factor for desorption is 10^{13} s^{-1} , then the residence time of an Au adatom on graphite is only 0.5 ms at 300 K. This value is consistent with the upper limit of 10 ms placed by Arthur and Cho [49]. For comparison, $E_{a,\text{metal}}$ of an Au adatom on unreconstructed Au(111) is 2.32 eV (Table 3), which corresponds to a residence time of at least 10^{27} s at 300 K.

Desorption cannot be the sole reason, however, for σ (or $\sigma') < 1$ for all metals on HOPG. For Pt, $E_{a,\text{graphite}} = 2.16$ eV (Table 1), so its residence time at 300 K should be very long— 10^{24} s —yet Howells et al. [85] found $\sigma < 0.1$. To reconcile these two points, one must conclude that the adsorption rate is very low, *independent* of the desorption rate, at least for Pt; in other words, many metal atoms are reflected without adsorbing.

Analysis of the residence time for Au, from a different perspective, leads to the same conclusion. A residence time of 0.5 ms at 300 K would allow a diffusing adatom to move ca. 20 μm , using a diffusion barrier of 0.010 eV (from Table 1). Thus, a diffusing Au atom would be captured at a step before it would desorb. So even for Au, which is one of the more weakly-bound metals, desorption is not sufficient to account for $\sigma < 1$.

In adsorption, the incident atom has a certain kinetic energy (at least equal to the thermal energy of the evaporator—of order a few tenths of eV). In order for adsorption to occur, this incident energy must be dissipated efficiently by the surface. Inefficient energy transfer (accommodation) may be the reason $\sigma < 1$ for metals on graphite. In contrast, there have been many studies of metal adsorption on graphene, but no indication that $\sigma < 1$ at 300 K, suggesting that the number of coupled carbon layers is crucial in energy dissipation.

In summary, reflection (without adsorption) must be considered as a possible pathway for metal atoms impinging on the basal plane of graphite. To our knowledge, there have been no studies of the dynamics of metal-graphite scattering, other than the

molecular beam work by Arthur and Cho [49]. Further investigations—including theoretical ones—would be enlightening, as well as comparisons of metal condensation on *graphite* vs. *graphene*.

Conclusions.

Metal adsorption and growth on the basal plane of graphite has been studied for many years. Experimentally, metals on graphite are surprisingly difficult to work with, due to (possible) effects of non-UHV environments, and difficulties in imaging with scanning probe techniques due to the relatively-low adsorption energy of the metals. In this review we have summarized some of the consistent observations, and pointed out some of the inconsistent ones as well. There are opportunities for clarification and expansion on many points—systematic trends in energetics of adsorption and diffusion for different metals, trends in energetics with the number of carbon layers (i.e. progressing from graphene to graphite), adsorption dynamics, and stability of 2D vs. 3D clusters. We think that there is a special opportunity for simulations and modeling to contribute to our understanding of these issues at this point in time.

More specifically, with regard to the adsorption energies, we propose that the adsorption energy of a metal on *graphite* is bracketed by its adsorption energy on *graphene*, and on itself. This relationship is consistent with values that are currently available, but bears further testing. This relationship leads directly to the expectation that metal clusters on graphite adopt 3D rather than 2D shapes. Hence, it is puzzling that there are several reports of (small) 2D clusters in the literature. These reports exist even for the coinage metals, where the driving force for 3D growth should be strongest.

A limited amount of DFT results suggests that the single-atom diffusion barrier on graphite terraces is greater than or comparable to the diffusion barrier on graphene. On graphite, step edges bind metal atoms more strongly than terraces. This energetic difference, plus the low terrace diffusion barrier, leads to facile decoration of steps. Preferential step decoration has been observed in many experimental studies, despite the possibility that step edges may also be preferential sites for impurities.

Finally, there are several indications that the condensation coefficient of a metal is not unity at 300 K. This may be due the tendency for the metal to reflect rather than adsorb. The dynamics of metal atom scattering, and how it is influenced by the number of carbon layers, warrants further investigation.

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Table 1. Values of $E_{a/\text{graphite}}$ calculated from DFT for various metals. Other parameters are diffusion barrier (ΔE), and charge transfer (Δq) relative the charge on the neutral adatom. Only calculated values using 2 or more carbon sheets are shown, with the exception of cases where 1-layer values were calculated in addition to the multi-layer values, since such cases illustrate trends. High-symmetry adsorption sites are on-top over α carbon (T_α), on-top over β carbon (T_β), top unspecified (T), bridge (B), and hollow (H). See Fig. 1. Note that the B site is sometimes named bond center site.

Metal	Ref	Method	No. of Carbon Layers	Corrected for Dispersion Forces?	Preferred Binding Site (see Fig. 1)	$E_{a/\text{graphite}}$ (in eV)	$\Delta E_{\text{graphite}}$ (in eV)	Δq (in eV)
Cr	[53]	DFT - GGA	1	yes	H	0.542	0.022	
			2		H	0.738	0.021	
			3		H	0.832	0.022	
Pt	[118]	DFT - LSDA	2	no	T_β /B	1.11 (both sites)		0.49(T_β) 0.46(B)
	[76]	DFT-optB88	4	yes	B	1.87	0.161	
Cu	[76]	DFT-optB88	4	yes	T_β	0.512	0.015	
Ag	[119]	DFT - LDA	2	no	T_β	0.54		0.26
	[120]	DFT - LDA	4	no	T_β	0.439		
	[76]	DFT-optB88	4	yes	T_β	0.282	0.006	
Au	[53]	DFT - GGA	1	yes	T	0.380	0.007	
			2		T_β	0.543	0.024	
			3		T_β	0.612	0.025	
	[52]	DFT - GGA	2	no	T	0.51	0.04-0.05	-0.14
	[121]	DFT - LDA	4	no	T_β	0.674	0.04-0.06	-0.165
	[122]	DFT - LDA	1 2	no	T T	0.66-0.89 0.68-0.80		
	[76]	DFT-optB88	4	yes	T_β	0.495	0.010	

Table 2. Comparison between the best available values of $E_{a/\text{graphite}}$ (selected from Table 1), $E_{a/\text{graphene}}$, and $E_{a/\text{metals}}$ (latter values given more fully in Table 3). All values come from DFT calculations. All calculations for $E_{a/\text{graphite}}$ include dispersion force correction.

Adatom	$E_{a/\text{graphene}}$ (in eV)	$E_{a/\text{graphite}}$ (in eV)	$E_{a/\text{metal}}$ (in eV)
Cr	0.187 [54]	0.832 [53]	3.41 [56]
Pt	1.552 [54]	1.869 [76]	4.60 [123] 4.50 [56]
Cu	0.227 [54]	0.512 [76]	2.27 [56]
Ag	0.021 [54]	0.282 [76]	1.91 [56]
Au	0.096 [54]	0.495 [76]	2.32 [56]

Table 3. Self-adsorption energies of some transition metals [56]. The adsorption site for adatoms on fcc, hcp, and bcc metals is assumed to be fcc, hcp, and long bridge, respectively. Values are calculated using DFT-PBE, averaging results from 3 to 5 layer slabs, with 4 surface atoms on each side of the clean slab [124].

fcc metal	$E_{a,\text{metal}}$ (eV)	hcp metal	$E_{a,\text{metal}}$ (eV)	bcc metal	$E_{a,\text{metal}}$ (eV)
Rh(111)	4.54	Ti(0001)	4.55	Ta(110)	7.00
Ir(111)	5.52	Zr(0001)	4.76	Cr(110)	3.41
Ni(111)	3.62			Mo(110)	5.54
Pd(111)	2.87			W(110)	7.41
Pt(111)	4.50			Fe(110)	4.42
Cu(111)	2.27				
Ag(111)	1.91				
Au(111)	2.32				

Figure captions.

Fig. 1. Schematic diagram of the (0001) plane, i.e. basal plane, of graphite. The ABA stacking pattern of graphite, also known as the Bernal polymorph, results in two types of surface carbon atoms, one sitting directly above a carbon atom in the layer beneath (labeled alpha (α)), and the other sitting above a void in the layer beneath (labeled beta (β)).

Fig. 2. STM images of clean graphite. (a) Smooth terraces. Image size is $2\ \mu\text{m} \times 2\ \mu\text{m}$, 0.1 V tip bias, 0.5 nA tunneling current. (b) Atomic-scale resolution. $3.4\ \text{nm} \times 3.4\ \text{nm}$, 0.08 V, 0.3 nA. (c) Extensive folds. $2\ \mu\text{m} \times 2\ \mu\text{m}$, 0.1 V, 0.5 nA. (d) Inclusion. $25\ \text{nm} \times 25\ \text{nm}$, 0.1 V, 0.3 nA.

Fig. 3. A sequence of two STM images over the same region of a graphite surface with Cu clusters, illustrating the changes that scanning can cause in metal clusters. Each image is $250 \times 250\ \text{nm}^2$, acquired with -0.8 V tip bias and 0.1 nA tunneling current.

Fig. 4. Morphology of various metals vapor-deposited on HOPG at 300 K unless otherwise specified. (a) Fe, reproduced from Ref. [83]; (b) Co, reproduced from Ref. [84]; (c) Ni (deposited at $< 200\ \text{K}$), reproduced from Ref. [125]; (d) Ag, reproduced from Ref. [63]; (e) Pt, reproduced from Ref. [85]; and (f) Au, reproduced from Ref. [77].

Fig. 5. STM images of small 2D clusters on HOPG which may be precursors to 3D island growth: a) Ag, reproduced from Ref. [67]; b) Au, reproduced from Ref. [67]; and Pt, reproduced from Ref. [99].

Fig. 6. Preferential decoration of HOPG step edges by various metals, vapor deposited at 300 K unless otherwise specified. (a) Ag, reproduced from Ref. [63]; (b) Pt, reproduced from Ref. [85]; (c) Pt, deposited by atomic layer deposition, reproduced from Ref. [16]; (d) Ru, reproduced from Ref. [109]; and (e) Au deposited at 673 K, reproduced from Ref. [88].

Fig. 7. HOPG steps on a nominally-clean surface, and associated line profiles. (a) Partially-contaminated step—most common type observed. $125\ \text{nm} \times 125\ \text{nm}$, -0.5 V (at tip), 0.2 nA. (b) Highly-contaminated steps—rarely observed. $250\ \text{nm} \times 250\ \text{nm}$, -0.6 V, 0.3 nA. (c) Uncontaminated steps. $250\ \text{nm} \times 250\ \text{nm}$, -0.5 V, 0.5 nA.

Fig. 8. Cu decoration at HOPG steps of various heights, and corresponding line profiles. All images are $250\ \text{nm} \times 250\ \text{nm}$. Numbers in profiles give carbon layer heights. (a) Left to right: 2-layer and 1-layer graphite steps. -1.5 V at tip, 0.3 nA. (b) 3-layer graphite step. -1.5 V, 0.3 nA. (c) 5-layer graphite step. -1.5 V, 0.1 nA.

Fig. 9. (a) SEM of Au-decorated vacancy loops at 56,000x. Reproduced from Ref. [25]. (b) STM of Au-decorated vacancy loops. Au was deposited at 623-673 K. Reproduced from Ref. [47].

Fig. 10. Time dependence of desorbing Cu flux, with a continuous Cu beam impinging on graphite at 300 K. The solid curve is the best fit to a model in which Cu atoms on graphite have high mobility and a limited lifetime, and can only adsorb irreversibly if they become incorporated at the periphery of 2D Cu islands. Reproduced from Ref. [49].

Fig. 11. Comparisons of metals deposited on a normal graphite surface (left) and on a graphite surface that was pre-sputtered (right). (a-b) Fe, from Ref. [83]; (c-d) Ag, from Ref. [63]; (e-f) Ru, from Ref. [109].

Fig. 1

Fig. 2

0.10 ML, -0.8 V, 0.1 nA

0.10 ML, -0.8 V, 0.1 nA

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Figure 10

Fe

Ag

Ru

Fig. 11