from academia as well as from industry. Without doubt it is also surprising to observe that a simple amino acid molecule—as described by List et al.—can, in principle, act like an enzymatic system, thus representing an efficient enzyme mimic.

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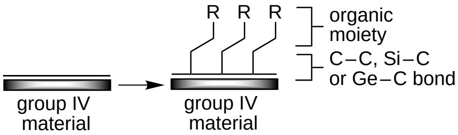
Diamond Surfaces: Just Big Organic Molecules?

Jillian M. Buriak*

While the organometallic surface chemistry of oxide-free semiconducting group IV materials has been dabbled in since the early 1960s,[1] an incredible explosion of interest and resources directed to this area has taken place in the latter half of the 1990s (Scheme 1).[2] Silicon has received the bulk of the attention because of its applications in micro- and optoelectronic devices, MEMs (microelectromechanical machines), and sensors, to name a few.[3] Derivatization through Si–C bonds appears promising due to the stability of this bond and to tap into the vast repertoire of known organic reactions that will allow for precise tailoring of surface characteristics and functions.[2] Recent work concerning silicon's heavier congener, germanium, appears to demonstrate similar reactivity patterns under ultrahigh vacuum (UHV) conditions to that of silicon, allowing access to Ge–C derivatized surfaces, although much research remains to be done to generalize this.[4]



Scheme 1. Modification of the surfaces of group IV elements.

The surface chemistry of silicon's more "northerly" and expensive neighbor, carbon in form of diamond, is even more poorly understood.[5] The chemistry of the unsaturated carbon allotropes, including C_{60} and carbon nanotubes, have been, and are, the subject of intense investigation.[6] Unfortunately, the inertness at room temperature and expense of studying diamond has inhibited the same level of fundamental research. Because of the unique characteristics of diamond, such as mechanical hardness, wide band gap, and optical transparency, among others, interest in diamond surface chemistry has both academic and potential technological appeal.[7]

One of the more pressing questions concerning diamond reactivity is whether its surface chemistry parallels that of Si(100) and Ge(100), or is it more similar to solution phase, molecular organic compounds? Certainly, molecular silicon and germanium compounds have differing reactivity from structurally similar carbon-based molecules in heterolytic reactions due to the availability of empty *n*d orbitals, which

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permits five- and six-fold coordination. Fascinating work from the groups of Bent at Stanford,[8] and Hamers at the University of Wisconsin, Madison,[9] in collaboration with researchers at the Naval Research Laboratory (NRL) in Washington D.C. and the GE Corporation, have shown that the surface chemistry of diamond under UHV conditions is analogous to that of molecular olefins and that, unlike the corresponding Si and Ge surfaces, the bulk material underneath has a weaker effect on the chemistry.

Like Si(100) and Ge(100) orientations, C(100) surfaces can undergo a 2×1 reconstruction under ultrahigh vacuum (10^{-10} Torr) conditions, yielding a surface with oriented carbon–carbon bonds (Figure 1). The two carbon atoms are linked by a σ- and a partial π bond, which endows the dimer with olefinic character. The ultimate test of the nature of the C=C bond is an examination of its reactivity: Will it react in a similar fashion to known, solution phase alkenes? As demonstrated by Bent and co-workers,[8] the surface reacts with the diene, 1,3-butadiene, to give a [4+2] cycloaddition as the major reaction pathway at room temperature, a Diels–Alder reaction by definition (Scheme 2a). An alternative [2+2] reaction is not observed with the diene or is only a minor product. Bent and co-workers had already demonstrated Diels–Alder-like behavior with dienes on oriented dimers on the Si(100) surface[10] and thus they confirm that the carbon and silicon surface chemistries under these conditions are similar and closely related to each other and to solution phase organic olefins.

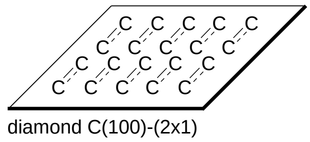
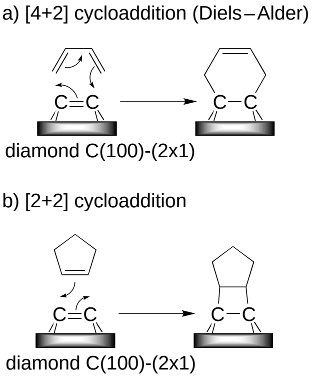


Figure 1. The ordered carbon–carbon dimers with partial double-bond character present on the reconstructed diamond C(100)-(2×1) surface, formed under UHV conditions.



Scheme 2. a) Diels–Alder reactivity on the reconstructed diamond surface with dienes, as demonstrated by Bent and co-workers. b) The [2+2] cycloaddition chemistry with olefins, studied by Hamer's group.

Because the Diels–Alder reaction yields an organic moiety with an isolated olefinic group, the potential exists to carry out further functionalization to produce more highly sophisticated surfaces. Unfortunately, the surface-bound olefin has not yet been coaxed to react with an additional molecule of 1,3-butadiene through a secondary Diels–Alder reaction, as might be expected from known organic reactivity; Diels–Alder reactions with dienes and an alkene lacking an electron withdrawing group require high pressures and temperatures to proceed.[11] It would be interesting to see if further chemistry carried out on this double bond produces doubly derivatized surface terminations.

In the same issue of the *Journal of the American Chemical Society*, Hamers and co-workers reported on the [2+2] reaction of olefins with the same C(100)-2×1 reconstructed diamond surface (Scheme 2b).[9] Such [2+2] cycloadditions between olefins are usually not observed as ground-state concerted reactions because they violate the Hückel $4n+2$ rule. These workers and others had previously shown, however, that this cycloaddition is very facile on the corresponding Si(100) and Ge(100) reconstructed surfaces and also terminated with unsaturated dimers.[4, 12] Their main motive for examining the reaction on diamond was to probe the reactivity differences between the elements—is the ease of the [2+2] reaction on silicon and germanium due to unusual chemistry unique to these elements or to the fundamental differences in reactivity between surface dimers and molecular analogues? Interestingly, they found that the [2+2] addition of cyclopentene takes place on C(100), as observed on Si(100) and Ge(100), but with a much lower probability (sticking coefficient is 10^{-3} smaller than that on silicon) because of a higher energy barrier. The lower activation energy of the Si(100) and Ge(100) surfaces, according to calculations made by Hamers et al., is due to a distortion of the dimers on these surfaces, in which the Si=Si and Ge=Ge species tilt out of the surface plane. This lowers the symmetry of the dimer, thus permitting the [2+2] addition to take place with a low energy barrier. On C(100), however, the dimers do not appear to tilt and, thus, a more concerted and unfavorable [2+2] addition must occur. This work indicates that the surface chemistry on group IV materials may differ from that of molecular analogues due to distortions induced from the underlying bulk, with diamond being most closely related to the solution phase species.

Overall, the reactivity trends suggest that the chemistry on the C(100) dimer diamond surfaces is very similar to that of molecular olefins. Si(100) and Ge(100) surfaces also have related chemistries but differ in that the underlying material distorts the surface dimers, thus lowering energy barriers and inducing subtle effects on the reaction mechanism. This chemistry also permits the diamond surfaces to be terminated with organic monolayers in a rational fashion. To summarize, this research is important not only for possible materials applications of diamond but also from a very fundamental perspective of surface reactivity as well.

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Olefin Polymerization by Late Transition Metal Complexes—A Root of Ziegler Catalysts Gains New Ground

Stefan Mecking*

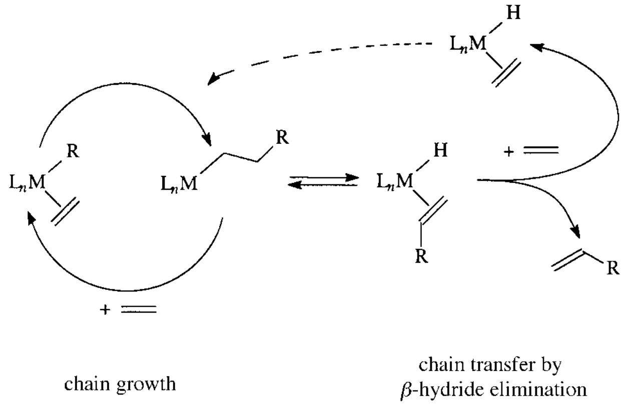
Introduction

Polyolefins are of vast economic importance, which is reflected by an annual production of more than 70 million tons of polyethylene and polypropylene. While the major portion of these materials is produced with Ziegler- and chromium-based catalysts, the older free-radical process that affords low-density polyethylene (LDPE) has maintained its significance.[1] Despite the necessity of working at over 1500 bar, 16 million tons of LDPE are currently consumed annually and new large plants continue to be built.[1d,e] One attractive feature of the high-pressure process is the possibility of incorporating functionalized olefins, such as vinyl acetate or acrylates. Incorporation of even small amounts of polar moieties can increase adhesion properties and compatibility of polyolefins with other materials. Another attractive feature is the different property profile of LDPE compared to the linear ethylene homo- and copolymers produced by Ziegler catalysts. In the free-radical polymerization of ethylene, short- as well as long-chain branches are formed without any added co-monomer. Short-chain branches affect polymer properties, such as crystallinity and melting temperature, and are important in controlling polyolefin application properties. Long-chain branches (typically containing 100 or more carbon atoms) particularly influence the rheology of polyolefin melts, and result in good processing properties of LDPE.

These considerations exemplify existing challenges for transition metal catalyzed coordination polymerization in low-pressure processes. In regard to the desirable incorporation of polar monomers, early transition metal based Ziegler catalysts and metallocenes are, unfortunately, highly sensitive to polar reagents. By comparison, late transition metal complexes are generally much more functional-group tolerant as a result of their less oxophilic nature. In addition, they can provide access to unique polyolefin branching structures. Recent discoveries of novel olefin-polymerization catalysts based on late transition metals represent major advances. These findings are highlighted and put into perspective with previous developments, by using ethylene polymerization as a guideline.[2, 3]

General Aspects of Catalyst Design

Polymerization of ethylene or α-olefins by Ziegler-Natta or metallocene catalysis and C–C linkage by late transition metal complexes rely on the same basic types of reactions, namely chain growth by migratory insertion in alkyl–olefin complexes and chain transfer by various mechanisms. However, late transition metal catalysts usually yield dimers or oligomers because of the propensity of alkyl complexes of late transition metals for chain transfer by β-hydride elimination (Scheme 1).[4, 5c] A prominent example is the Shell Higher Olefin Process (SHOP), developed by Keim et al. in the 1960s and 1970s, in which linear α-olefins are obtained by nickel-



Scheme 1. Simplified schematic representation of ethylene oligomerization and polymerization by late transition metal (M) complexes (R = growing polymer/oligomer chain).

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