Stability of Scanning Tunneling Microscopy Tip-Induced Bimetallic Nanoclusters: Influence of Hardness and Composition on the Cohesive Energies

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The stability of bimetallic nanoclusters fabricated using scanning tunneling microscopy methods is investigated using a phenomenological formalism, and the cohesive energies of Au–Cu, Au–Pd, and Ag–Cu systems are estimated. The influence of chemical hardness, composition of the substrate, and metal adatoms in the nanocluster as well as the dissociation energies of S–S and S–M bonds as regards the stability of nanoclusters is demonstrated.

1. Introduction

The field of nanomaterials constitutes a frontier area of research in view of its potential applications in microelectronic devices[1,2] and catalytic processes.[3] While diverse approaches to the fabrication of nanowires, nanoclusters, etc. are being intensively pursued,[4] the factors governing their stability are not yet clearly understood. Electrochemical fabrication processes for surface structures of micrometer sizes have been extensively investigated during the past decade.[5–8] On the other hand, the study of nanoclusters using electrochemical techniques is of recent origin.[9–11] In this respect, the tip of a scanning tunneling microscope (STM) acts as a powerful tool[8,12–16] for the formation of nanostructures on different substrate surfaces. This tip-induced method when employed at metal/electrolyte interfaces creates surface coordination imperfections on the metal, during the application of large voltage pulses (of duration ranging from microsecond to nanosecond) between the tip and substrate metal.[5–8] These surface coordination imperfections then act as the nucleation centers for the nanoclusters. The deposition of Cu clusters on the Au(111) surface acts as a prototype for the electrochemical fabrication of nanoclusters. In contrast to the anticipation that clusters are less stable than the corresponding bulk material, copper clusters on the Au(111) surface are stable even at the dissolution potential of bulk copper.[10,11] This has been attributed to (i) the difference in the quantum confinement of the electronic levels in the bulk metal and the nanoclusters[11] and (ii) Cu–Au alloy formation.[17]

The objectives of this paper are (i) to evaluate the cohesive energies of nanoclusters formed using STM techniques and interpret their stability, (ii) to demonstrate the usefulness of the concept of chemical hardness in analyzing the formation of alloys of two-component nanosystems, and (iii) to estimate the composition of the nanoclusters formed between two metals with the help of the cohesive energies.

2. Formation and Stability of Nanoclusters

Among various methods of fabrication of nanoclusters, the methodology employing the underpotential deposition (UPD) is especially attractive insofar as a controlled formation as well as structural characterization is possible.[17] In UPD, a (sub)-

monolayer of the depositing species is formed on the substrate at potentials less positive to the reversible Nernst potential.[18] It may be recalled that the occurrence of the UPD in itself is selective since the work function differences and different interaction energetics play a crucial role.[19,20] In the present context, one may envisage the following factors to influence the formation of nanoclusters involving a substrate and the depositing species viz. (i) binding energies between substrate atoms and substrate-depositing species, (ii) corresponding compositions, and (iii) work function vis a vis chemical hardness of the substrate and the depositing metal.

2.1. Formulation of Cohesive Energies for Nanoclusters. The cohesive energies of metals and alloys may be computed using diverse types of local density approximations, and extension of these to nanoclusters is being attempted.[21] An alternate phenomenological approach[22] envisages a formal expression for the cohesive energy E_c in terms of the diameter of the metal atom (d), that of the nanocluster (D), and surface energy of the bulk metal (γ_0) viz.

$$E_c = k\pi N_A \gamma_0 d^2 \left(1 - \frac{d}{D}\right) \qquad (1)$$

where N_A is Avogadro's number and the proportionality constant k is equal to unity in general.[22] While the above equation incorporates the salient geometrical factors as well as the surface energy of the bulk metals, it is inadequate to investigate the energetics when different compositions of nanoclusters can be fabricated by suitable experimental protocols. It is hence preferable to formulate parametric equations, albeit phenomenologically for computing the cohesive energies and demonstrate their qualitative and quantitative validity, for hitherto available data. This would then enable a systematic investigation of the thermodynamic stability of nanosystems in general.

In modern applications of density functional theories for diverse chemical reactions, the concept of chemical hardness (η) has been shown to be an attractive viewpoint in (i) predicting the specificity and selectivity of several types of processes[23–26] and (ii) interpreting[27] electrode kinetic data using hardness. The crux of these investigations is that the greater the differences in hardness between the reactants and products the greater will be the rate of the reaction.[26] Extending this principle further, it is reasonable to suppose that the difference in the chemical

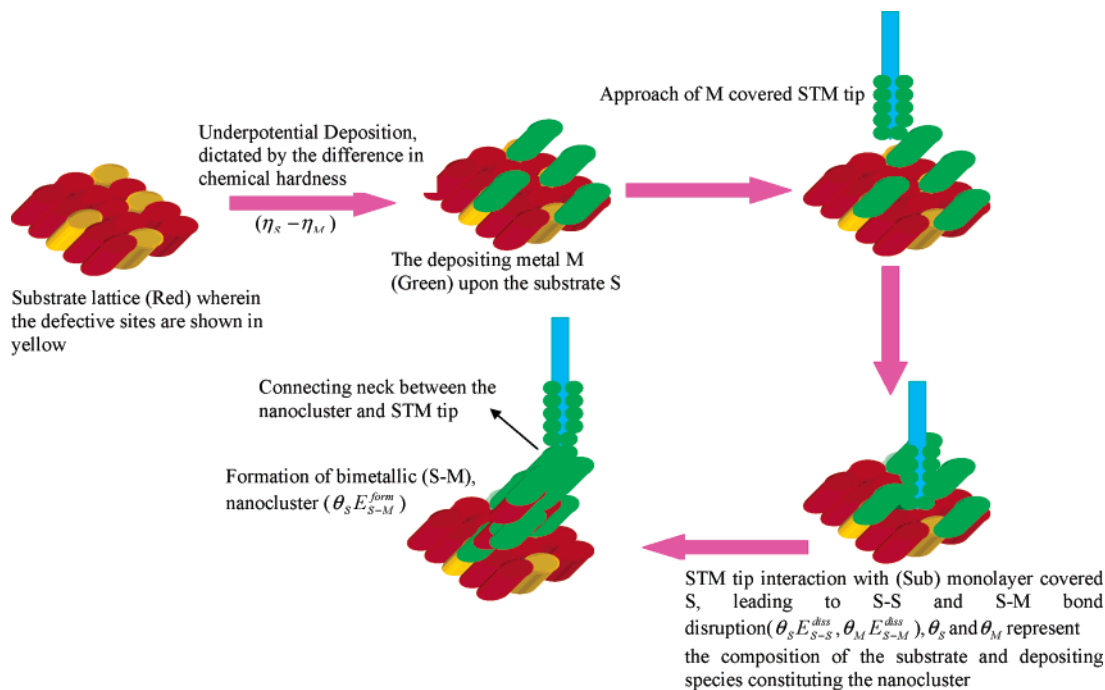* To whom correspondence may be addressed. E-mail: mvs@chem.iitm.ac.in.

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Figure 1. Representation of the processes involved in the formation of bimetallic nanoclusters via STM tip-induced method leading to the formulation of eq 3.

hardness between the substrate (S) and adatom (M) will directly influence the cohesive energy. Thus

$$E_c = (\eta_S - \eta_M) + \text{terms involving compositions of}$$
$$\text{metals and bond energies} \quad (2)$$

The additional terms arising in eq 2 may be deduced from the fact that, in the formation of nanoclusters between two metals (S and M), the dissociation energies pertaining to S—M and S—S bonds along with the S—M bond formation energy should occur (cf. Figure 1). Hence eq 2 is rewritten as

$$E_c = (\eta_S - \eta_M) + \theta_S E_{S-S}^{diss} + \theta_M E_{S-M}^{diss} + \theta_S E_{S-M}^{form} \quad (3)$$

where θ_M and θ_S denote the fraction of the depositing metal and the substrate involved in the nanocluster formation and $(\theta_M + \theta_S)$ equals unity. Further, noting that $E_{S-M}^{form} = -E_{S-M}^{diss}$, eq 3 becomes

$$E_c = (\eta_S - \eta_M) + \theta_S E_{S-S}^{diss} + (\theta_M - \theta_S) E_{S-M}^{diss} \quad (4)$$

Equation 4 provides a direct relationship among parameters such as the fraction of metal atoms forming the nanocluster, chemical hardness differences, and dissociation enthalpies of S—M and S—S bonds. The parameters θ_S and θ_M are defined as the fraction of the substrate metal and the depositing metal involved in the nanocluster formation viz.

$$\theta_M = \frac{\text{number of M atoms in the cluster}}{\text{total number of atoms in the cluster}} \quad (5)$$

and

$$\theta_S = \frac{\text{number of S atoms in the cluster}}{\text{total number of atoms in the cluster}} \quad (6)$$

In eq 4, the difference in chemical hardness indicates the kinetic stability of the nanoclusters, whereas the energetics terms incorporate the thermodynamic stability of the nanoclusters.

In the case of pure clusters (where the substrate and the depositing metals are identical), eq 4 becomes

$$E_c = \theta_M E_{M-M}^{diss} \quad (7)$$

Even when the substrate metal is a single crystal, the depositing metal being polycrystalline, eq 4 is still valid albeit with modifications pertaining to the chemical hardness values and various energetic terms. Thus the cohesive energy of the pure clusters is influenced by the strength of different types of metallic bonds. The rationale behind the postulate of eq 3 arises from the following features: (i) the difference in hardness between the substrate and the depositing metal influences the cohesive energy; however, terms involving θ_S and θ_M do not accompany the term $(\eta_S - \eta_M)$, in view of the fact that this term constitutes the initial stage in the formation of nanoclusters viz. (sub)-monolayer formation of M on S; (ii) the second term E_{S-S}^{diss} takes into account the energetics associated with the disruption of the S—S bonds on the substrate lattice caused by the interaction of the STM tip with the substrate. Since only a fraction of the substrate lattice sites (governed by θ_S) get disrupted due to the interaction with the STM tip, the term E_{S-S}^{diss} needs to be multiplied by θ_S; (iii) after the formation of a (sub)-monolayer of M on S, S—M bond dissociation (E_{S-M}^{diss}) occurs, on account of the interaction with the STM tip. However, the nanoclusters are formed only on those fraction of sites (θ_M), wherein the STM tip interacts with the substrate covered by depositing metal, hence E_{S-M}^{diss} is multiplied by θ_M; (iv) as the STM tip is pulled away from the metal-covered substrate surface, the substrate and the depositing metal form bimetallic nanoclusters, leading to the incorporation of the term E_{S-M}^{form}. Further, since the alloy-forming ability of the substrate metal with the depositing metal dictates the stability of the nanoclusters, the fraction of the substrate metal constituting the nanocluster plays a crucial role; hence multiplication by θ_S is required. Figure 1 depicts a representation of the above factors.

2.2. Estimation of the Cohesive Energy of Nanoclusters. Equation 4 constitutes a simple phenomenological expression

TABLE 1: Kinetic and Thermodynamic Stability of Nanoclusters from Eq 4

nanocluster	$(\eta_S - \eta_M)$ in eV	eneregetic parameters of eq 4 in eV	E_c in eV	kinetic stability from the hardness difference	thermodynamic stability from the energetics of eq 4	remarks
Au − Cu	0.22	1.62	1.74	moderate	high	Formation of the nanocluster is facile, and the stability is high.
Au − Pd	0.43	1.53	1.81	high	moderate	The formation of the Au−Pd nanocluster is more facile due to higher values of $(\eta_S - \eta_M)$ as compared with the Au−Cu nanocluster, but less stable than the Au−Cu nanocluster due to lower values of the energetics. Hence the chemical hardness difference predominates in this case.
Ag − Cu	−0.11	1.78	1.38	very low	very low	Formation of the nanoclusters itself is not facile and hence Ag−Cu nanoclusters have the least stability among Au−Cu, Au−Pd, and Ag−Cu systems.

for computing the cohesive energies of nanoclusters which incorporates the composition of the nanoclusters *in terms of the fraction of the substrate and the depositing species*. Its applicability to a few recently studied systems are discussed below:

(i) Au(111)−Cu Nanocluster. The substrate in the case of the copper−gold nanocluster is Au(111), while the depositing species is Cu. The chemical hardness of Au(111) and Cu has been evaluated as 3.46[27] and 3.25 eV,[28] respectively. Since the dissociation energies of the depositing species with the single crystals are in general unavailable, we use the corresponding estimates pertaining to the polycrystalline metals. Hence the dissociation energies Au−Au and Au−Cu are employed as 2.24[29] and 2.36 eV,[29] respectively. Although the fractions θ_S and θ_M are in general unavailable, in a recent molecular dynamics simulation,[17] a Au−Cu nanocluster consisting of 26 Cu atoms and 11 Au atoms was noticed, thus yielding $\theta_M = 0.7$ and $\theta_S = 0.3$. By employment of the above parameters, eq 4 yields the cohesive energies of Au−Cu nanoclusters as 1.83 eV. It is interesting to estimate E_c of the Au(111)−Cu nanocluster using eq 1 of Chen et al.[22] The atomic diameter of the metal (d) and that of the nanocluster (D) has been deduced as 280 pm[29] and 3 nm,[13] respectively. The surface energy of bulk copper is reported[30] as 1.295×10^{-5} eV m^{-2}. Hence the cohesive energy of Au−Cu nanocluster follows from eq 1 as 1.74 eV, in satisfactory agreement with the value of 1.83 eV estimated using eq 4.

(ii) Au−Pd Nanocluster. To compute E_c of the Au−Pd nanocluster from eq 4, the fractions θ_M and θ_S are required. Since these are unavailable, we first estimate E_c using eq 1 (in view of the satisfactory agreement in the case of the Au−Cu nanocluster as shown above) and employ this value of E_c to deduce θ_M and θ_S using eq 4. The values of d and D pertaining to the Au−Pd nanocluster are 420 pm[29] and 1 nm,[13] respectively, and the surface energy of bulk Pd is reported[30] as 1.71×10^{-5} eV m^{-2}. Hence, the cohesive energy of the Au−Pd nanocluster is calculated as 1.81 eV. The dissociation energies of Au−Au and Au−Pd have been employed as 2.24 and 1.41 eV, respectively, from tabular compilations.[29] The chemical hardness values of Au(111) and Pd are 3.46[27] and 3.03 eV.[28] Incorporating the above parameters and E_c as 1.81 eV deduced above, eq 4 yields the composition of Au−Pd nanocluster as $\theta_{Pd} = 0.84$ and $\theta_{Au} = 0.16$.

(iii) Ag−Cu Nanocluster. In an analogous manner, using the values of d and D as 280 pm[29] and 1.5 nm,[13] respectively, and the surface energy of bulk copper as[30] 1.295×10^{-5} eV m^{-2}, the cohesive energy of the Ag−Cu nanocluster has been deduced as 1.56 eV from eq 1. By use of the dissociation energies[29] of

Ag−Ag and Ag−Cu as 1.66 and 1.80 eV, respectively, and the chemical hardness values of Ag(111) and Cu as 3.14[27] and 3.25 eV,[28] the composition of metals in Ag−Cu nanocluster viz. θ_{Cu} and θ_{Ag} is deduced from eq 4 as 0.92 and 0.08 from the number of atoms of copper and silver reported as 22 and 2, respectively, constituting the cluster.[13]

2.3. Kinetic and Thermodynamic Stability of Nanoclusters. An intriguing issue in the investigation of nanoclusters constitutes their kinetic and thermodynamic stability. The experimental studies involving STM,[8,13−16] ultrahigh vacuum (UHV),[31−33] and molecular dynamics simulations[36,37] indicate that Au−Cu and Au−Pd nanoclusters are more stable than Ag−Cu. It is of interest to inquire whether the above formalism is able to interpret the above features. It can be noticed that as the *difference in chemical hardness* values viz. $(\eta_S - \eta_M)$ decreases (as 0.43, 0.22, and −0.11 eV for Au−Pd, Au−Cu, and Ag−Cu, respectively), the cluster-forming ability increases in the series Ag−Cu, Au−Pd, and Au−Cu (cf. Table 1). This inference concerning the stability of nanoclusters is consistent with the experimental observations,[38] Monte Carlo simulations,[39] and molecular dynamics simulations.[17,39] Further, the cohesive energy is the energy required to separate the metallic crystal into individual atoms. Thus the higher the value of E_c, the more stable will be the nanocluster. Hence Au−Pd and Au−Cu clusters having higher values of E_c (1.81 eV and 1.74 eV) are more stable than Ag−Cu with a cohesive energy of 1.38 eV. Hence Table 1 demonstrates an interplay of several factors in dictating the kinetic and thermodynamic stability of the nanoclusters.

Apart from the influence of hardness and energetics and the θ_M and θ_S values, the composition of the nanocluster plays a crucial role; for example, in the case of Au−Cu nanocluster, the values of θ_M and θ_S are 0.7 and 0.3 ($\theta_S \approx \theta_M/2$), whereas in Ag−Cu as well as in Au−Pd, it is θ_M (0.84 in Au−Pd and 0.93 in Ag−Cu) that predominates and not θ_S (0.16 in the case of Au−Pd and 0.07 for Ag−Cu). Although the composition of the nanoclusters obtained by the combination of eqs 3 and 4 does not have any direct experimental evidence, the phenomenological nature of eq 4 provides a framework for comprehending the energetics of bimetallic nanoclusters at various compositions and interpreting their stability. Thus, it follows that the stability of the nanoclusters may be controlled by a proper variation of the composition of substrate and the depositing metal. Taking into account the errors involved in the hardness values and the tabulated dissociation energies, an error of ca. 1−4% may arise in the cohesive energies evaluated herein.

3. Summary

An explicit phenomenological relationship for the computation of cohesive energies of nanoclusters incorporating various bond energies, composition of the nanocluster, and chemical hardness values of the constituent species is proposed. The stability associated with Au−Cu, Ag−Cu, and Au−Pd nanoclusters is interpreted using the proposed formalism.

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