THEORETICAL STUDIES OF SURFACE REACTIONS
ON METALS AND ELECTRONIC MATERIALS

Report

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I. Research Scope

The objective of this research is the development and application of theoretical techniques that will provide a molecular level understanding of surface processes. These studies of surface phenomena involving adsorbate structure, energetics and reaction mechanisms relate to two different areas: electronic materials and transition metal catalysis.

In order to achieve accurate energetics for surface reactions, first-principles calculations are performed using a cluster embedding theory. This permits an accurate many-electron treatment of the adsorbate/surface portion of the system while coupling this region with the bulk. Calculations are carried out for the full electrostatic Hamiltonian (except for core electron pseudopotentials), with wavefunctions constructed by self-consistent-field (SCF) and configuration interaction (CI) expansions.

The projects dealing with hydrocarbon reactions and CO adsorption and dissociation on nickel and iron address fundamental questions related to surface reactivity. The study of the dissociation of methane on a nickel surface containing an iron atom is relevant to the use of methane for synthesis of other hydrocarbons and to the general topic of alkane reactivity. Studies of oxygen and sulfur containing compounds are designed to aid in the interpretation of structural and spectroscopic experiments. Silicon surface studies focus on several questions related to chemical vapor deposition reactions and growth of electronic materials. In collaborative work with experimental groups at N.C. State developing diagnostic techniques for monitoring film growth, influences on second harmonic generation arising from chemical modifications of interfaces are explored. The project involving diamond growth, carried out in collaboration with an experimental group at the Research Triangle Institute, explores factors that influence the bonding of carbon to nickel surfaces and surface reactions on carbon. Studies of defects produced by H atom migration in amorphous silicon are related to the degradation of the photovoltaic properties of this material on continued exposure to light.

II. Progress During Grant Period

In order to obtain accurate energetics of surface reactions, we have developed an *ab initio* formulation of the cluster embedding problem that uses localized orbitals to define an electronic subspace encompassing the adsorbate and neighboring surface atoms. In this way it is possible to treat the adsorbate/surface portion of a system accurately while coupling this region to the bulk lattice. Calculations are carried out for the full electrostatic Hamiltonian of the system (except for core electron pseudopotentials), and wavefunctions are constructed by self-consistent-field (SCF) and multi-reference configuration interaction (CI) expansions. Details of the procedure have been described in previous reports. Numerous applications to chemisorption and reactions on transition metal surfaces have been reported and those completed during the present grant period are summarized in a subsequent section.

Calculations on adsorbate/metal systems typically provide the following information as a function of surface site and adsorbate geometry:

- total energy (E)
- adsorption energy (ΔE relative to infinite separation from the surface)
- total wavefunction, electron densities
- ionization potentials and work function
- inner shell or core electron excitation energies
- vibrational frequencies
- dipole moments, dynamic dipoles

Knowledge of the energy as a function of the coordinates of the species undergoing reaction allows calculation of the equilibrium geometry, minimum energy reaction pathway and transition state energy.

One of the first objectives in our work was to treat the adsorption of simple adsorbates on metal surfaces in order to understand experiments in which adsorption sites were well characterized and to uncover the principal interactions that govern bonding between surfaces and adsorbed species. Several of the studies fall into this category. Although the electrons in the metal are delocalized, one of the early observations was that

the strong interactions, typically on the order of 30 - 100 kcal/mol, between nonmetal adsorbates and the surface split out a set of orbitals that could be regarded as localized in the vicinity of the adsorption site. The interaction between the metal s, p electrons and nonmetal adsorbates are found to be the principal contributor to the energetics of metal-adsorbate bonding. Metal d orbital - adsorbate orbital interactions are also important in transition metal systems, but even for these systems most of the adsorption energy comes from the s, p interactions.

Studies of a variety of adsorbates on nickel have now been completed leading to a better understanding of surface sites at which reactions occur. Work was completed on the reaction of methane with a Ni(111) surface containing a substitutional iron atom. The presence of the surface Fe atom substantially reduces the activation barrier for CH₄ dissociation to ~5 kcal/mol. Studies of the chemisorption H₃C-O- and H₃C-S- on Ni(111) and Ni(100) and the interaction of methoxy with coadsorbed CO have been completed along with studies of the behavior of dynamic dipoles and adsorbate vibrations as a function of surface site.

In order to illustrate the capabilities of the theoretical method, we shall report in this section results obtained for the methoxy / nickel system. References to studies of other adsorbate - metal systems are found at the conclusion of the section. For the adsorption of methoxy on Ni(111), the embedded cluster calculations give adsorption energies of 90 kcal/mol (three-fold site), 87 kcal/mol (bridge site) and 61 kcal/mol (atop site). At the three-fold site CH₃O is nearly perpendicular to the surface, consistent with the HREELS, UPS and FTIR experiments. The calculated energy increase of only 1.7 kcal/mol for a 30° tilt suggests a floppy CH₃ motion that could easily be influenced by adsorbate-adsorbate interactions. Adsorption at the bridge site is only 3 kcal/mol higher in energy and, in this case, the methoxy C-O axis is tilted away from the surface normal by 20°. The small energy difference means that both sites could be populated.

For CH₃O adsorbed at a three-fold site, the calculated C-O stretching frequency is 1025 cm⁻¹. This value is in good agreement with a value of 1027 cm⁻¹ recently obtained using IR and the value of 1040 cm⁻¹ observed using EELS. The calculated CH₃O-surface

perpendicular stretching frequency of 495 cm^{-1} is also consistent with a value of 500 cm^{-1} from EELS measurements.

Methoxy adsorption on Ni(111) is similar to hydroxyl adsorption. For OH adsorbed at a three-fold site, the calculated adsorption energy is 87 kcal/mol with the O-H axis inclined 10° away from the surface normal. The 10° tilt stabilizes the OH by only 2 kcal/mol. The calculated Ni-O equilibrium distance is $1.51\text{ \AA}$ and the HO-surface stretching frequency is 476 cm^{-1} .

Recent LEED studies of methoxy on Ni(111) by Bradshaw et al. [Surf. Sci. 304 (1994) 74; 331/333 (1995) 201] provide an opportunity to assess the accuracy of the quantum mechanical prediction of the geometry. Both theory and experiment agree on the preferred adsorption site and a geometry in which the C-O axis is essentially normal to the surface. The calculated O - Ni distance between nuclei, $2.07\text{ \AA}$, is longer than the $1.93\text{ \AA}$ from LEED, and this is likely due to a local reconstruction of the surface in which the LEED study shows the three nickel atoms bonded to the adsorbate are slightly lifted out of the surface by $0.1\text{ \AA}$. The LEED results also show a relaxation horizontally away from the oxygen by $0.11\text{ \AA}$. In the theoretical work, the Ni atoms are taken at their ideal positions corresponding to the bulk lattice. Methoxy on nickel has large ionic character, but, as with similar systems in which oxygen is directly bonded to the surface, the three-fold and bridge adsorption sites are preferred. At the bridge site, the C-O axis tilts by 20° and this makes the site competitive, but still higher by 3 kcal/mol compared to adsorption at the three-fold site. The vibrational frequency associated with the methoxy-surface stretch varies from 380 cm^{-1} at the bridge adsorption site (tilted methoxy) to 495 cm^{-1} at the three-fold adsorption site (untilted); the latter value is in agreement with EELS measurements. When CH_3O bonds to nickel, charge is transferred from the metal to CH_3O ; very small clusters cannot support the charge transfer and, consequently, the calculated CH_3O adsorption energy is less for such models.

Similar calculations for CH_3S adsorbed on Ni(111) show that both perpendicular and tilted geometries are possible. At the three-fold site, the C-S axis of CH_3S is nearly perpendicular and the adsorption energy is 62 kcal/mol; at the bridge site, the C-S axis is

tilted 45° and the adsorption energy is unchanged, 62 kcal/mol. Thus, methane thiolate exhibits a dramatic two-geometry energy degeneracy. For the atop Ni site, the adsorption energy is higher and the C-S axis is tilted 55° .

Embedded cluster calculations on two other adsorbate-nickel systems, HCO on Ni(100) and CN on Ni(111), show a distinctly different behavior of these species, compared to others with unsaturated valence, in that the atop atom adsorption sites are comparable in stability to the higher symmetry sites. Studies of the charge distribution by examining the variation of the dipole moment of the system with changes in the carbon-metal surface distance show a linear variation in dipole moment with a slope approximating unity (in a.u.). This is indicative of adsorption with strong ionic contributions. In these molecules, the electron transfer to carbon from the surface offsets some of the directionality of the bonding. For formyl, the adsorption energies are essentially the same at atop, bridge and four-fold sites, namely 63.5 ± 0.1 kcal/mol. For CN, the adsorption energies on Ni(111) are 113, 114 and 115 kcal/mol for atop, bridge and three-fold sites, respectively. Thus, these species follow the adsorption rules for lone pair adsorbates on nickel, and the flat interaction potential implies much greater surface mobility. One very interesting feature of the formyl system is the geometry change that takes place at different sites: for the four-fold and bridge sites, the C-O bond is parallel to the surface, while for adsorption at the atop Ni site the C-O axis tilts to give an angle of 110° with the surface normal. A large decrease in dipole moment accompanies the transition to the atop site with the C-O axis tilt.

Calculations on the methoxy/nickel and methanethiolate/nickel systems, particularly dynamic dipole and core ionization calculations, were found to be of value in interpreting current experimental work. Some of these investigations were carried out in collaboration with experimentalists at other institutions. Coadsorption studies of CO and H_3CO on Ni(111) revealed large effects of CO on the methoxy geometry and adsorption energy. The results of these and other studies have allowed semiquantitative rules to be formulated that describe the behavior of a broad class of adsorbates on metals and the effect of coadsorbed species.

In mechanistic studies of silane decomposition on the Si(100)-2x1 surface, a low energy pathway is found for the reaction $\text{SiH}_4 = \text{SiH}_3 + \text{H}$. A multi-step mechanism for the desorption of H_2 from Si(100)2x1H which involves a defect mechanism for forming a dihydride, SiH_2 , is proposed to explain experimental observations. Activation energy barriers were determined for the reaction of CH_4 and CH_3F with Si(111) and a new interpretation of supersonic beam experimental data is proposed based on the kinetic energy of two-atom components of the molecules colliding with the surface.

Work on silicon systems also included studies of impurities and dopants at the Si/SiO₂ interface, metastable defects, factors that affect optical second harmonic generation and H bonding linkages in amorphous silicon. In studies of the degradation of the photovoltaic properties of amorphous silicon alloys, an explanation of the Staebler-Wronski effect is proposed. The model involves a H-exchange reaction in which trapping of photo-generated holes promotes a transfer of the H atom from a -SiH group to a nearest-neighbor -Si-NH-Si- creating a Si-dangling bond and a metastable $(-\text{Si-NH}_2-\text{Si}-)^+$ group. Calculations indicate that neutral $(-\text{Si-NH}_2-\text{Si}-)$ is unstable, so that relaxation of $(-\text{SiNH}_2-\text{Si}-)^+$ groups can occur by trapping of a thermally released (trapped) electron during a thermal anneal.

In studies of the possibility of nucleating diamond on nickel, subsurface Na is discovered to stabilize tetrahedrally bonded carbon whereas subsurface C facilitates the formation of planar configurations of CH_3 and C_6H_6 on Ni(111).

Mechanistic studies of CVD reactions of CH_x with C(100) surfaces were carried out as part of an investigation of the potential use of carbon rich species in diamond growth. Factors that influence surface reconstruction and barriers to adsorption were examined. This is a field in which many semiquantitative calculations of reaction energetics have been reported in an attempt to elucidate factors that affect the quality of diamond films. The present *ab initio* configuration interaction calculations provide useful benchmarks for calibrating semiempirical methods as well as providing accurate results for elementary reactions on cluster models of the carbon surfaces.

Results on current projects and abstracts of papers published or submitted during

the grant period are included in Section III.

III. Results and Abstracts of Papers During 1993-96

1. Dissociative Adsorption of H₂ on Ni(111)

H. Yang and J. L. Whitten, J. Chem. Phys. **98**, 5039 (1993).

Abstract: *Ab initio* configuration interaction calculations are performed to study the dissociative adsorption of H₂ on a Ni(111) surface. The lattice is modeled as an embedded three-layer, 41-atom cluster. Ni 3d orbitals are explicitly included on seven Ni atoms on the surface. H is preferentially chemisorbed at a 3-fold site on Ni(111) and the calculated binding energy of 62 kcal/mol, H-Ni distance of 1.86 Å, and H vibrational frequency of 1176 cm⁻¹ are in excellent agreement with experimental data. H adsorbed at bridge and on-top Ni sites is 2.5 and 8.1 kcal/mol less stable, respectively. The heat of reaction H₂ (gas) → 2 H (ads) is calculated to be 22.0 kcal/mol exothermic. When two H atoms are adsorbed as nearest neighbors to the same Ni atom, 3-fold sites are preferred with H atoms adsorbed at fcc-fcc, hcp-hcp or across atom fcc-hcp sites. These structures are consistent with the observed (2x2)-2H LEED pattern. The average adsorption energy per H is calculated to be 62 kcal/mol for the across atom case. Adsorption of H at a 3-fold site on Ni(111) has a tendency to block adsorption at adjacent 3-fold sites; coadsorbed H atoms at adjacent sites are unbound by 15.5 kcal/mol relative to H₂ at infinite separation. For three H atoms chemisorbed at separated 3-fold sites sharing a Ni atom with the equal H-H lateral distances of 2.48 Å, the calculated average adsorption energy is 60 kcal/mol per H. Dissociation of H₂ at an on-top Ni site has the lowest activation barrier of 1.6 kcal/mol. For the transition state, the H-H bond length, H-surface height, and H-H vibrational frequency are 1.22 Å, 1.38 Å, and 2506 cm⁻¹, respectively. Molecular H₂ adsorbed over an on-top site is bound by 3.4 kcal/mol with a slightly stretched H-H bond length of 0.79 Å, H-surface height of 1.85 Å, and H-H stretching frequency of 3396 cm⁻¹.

2. Theoretical Studies of H₂ Desorption from Si(100)-2x1H

Ze Jing and J. L. Whitten, J. Chem. Phys. **98**, 7466 (1993).

Abstract. Theoretical studies of H₂ desorption from a cluster model of the Si(100)-2*1H surface show that the desorption pathway is symmetrical and has a desorption energy barrier of 3.75 eV and a corresponding adsorption energy barrier of 1.15 eV. The proper treatment of electron correlation lowers the desorption energy barrier considerably. The present results suggest that the desorption of two hydrogen atoms from different Si atoms of a surface dimer is not the desorption pathway observed experimentally at activation energies in the range 2.0 - 2.9 eV.

3. Reaction of CH₄ with Substitutional Fe/Ni(111)

H. Yang and J. L. Whitten, Surf. Sci. **289**, 30 (1993).

Abstract: The reaction of CH₄ with a substitutional Fe/Ni(111) surface is treated using a many-electron embedding theory, modelling the lattice as a 41-atom, three layer cluster. *Ab initio* valence orbital configuration interaction (multiple parent) calculations carried out

on a local surface region permit an accurate description of bonding at the surface. The 3d orbitals are explicitly used for the Fe atom and six nearest neighbor Ni atoms in the local surface region. The calculated activation energy for CH_4 dissociation at an atop Fe site to produce CH_3 and H coadsorbed on the surface is 5.7 kcal/mol, compared with 16.7 kcal/mol on Ni(111). The reaction of $\text{CH}_4 \rightarrow \text{CH}_3(\text{ads}) + \text{H}(\text{ads})$ is predicted to be 4 kcal/mol exothermic on the Fe/Ni(111) surface and the immediate dissociation products are CH_3 and H coadsorbed at across atom 3-fold sites. Across bond dissociation is energetically very unfavorable. The bonding properties of coadsorbed CH_3 and H on the Fe/Ni(111) surface are similar to those on Ni(111) surface. Compared to the clean Ni(111), the substitutional Fe/Ni(111) surface is very effective in activating CH_4 .

4. Mechanism of H_2 Desorption from Monohydride Si(100)-2x1H

Ze Jing, G. Lucovsky and J. L. Whitten, Surf. Sci., **296**, L33 (1993).

Abstract. Most recent experimental work on H_2 desorption from the monohydride Si(100) surface seems to point to a pairwise desorption mechanism involving the concerted desorption of two hydrogen atoms on different Si atoms of a single dimer. Using *ab initio* SCF and CI theory and a cluster model of the surface, the present work finds that the lowest energy pathway is symmetric rather than asymmetric. The desorption energy barrier is calculated to be 3.7 eV. Compared with an experimental value of 2.6 eV, the large barrier suggests that this direct desorption mechanism is not applicable. A multi-step desorption mechanism which involves a delocalized process in the formation of dihydride SiH_2 and a localized desorption of H_2 is proposed and is shown to explain the experimental observations.

5. Effects of Subsurface Na, H and C on the Bonding of Carbon to Nickel Surfaces

H. Yang, J. L. Whitten, and R. J. Markunas, Surf. Sci. **294**, L945 (1993).

Abstract: This paper reports the results of a theoretical study of Na, H and C subsurface atomic species in nickel and demonstrates how these interstitial atoms influence the reactivity of the Ni(111) surface and the structure of carbon species adsorbed on the surface. The benzene molecule, C_6H_6 , in planar and nonplanar geometries, is used to probe bonding at the surface. Adsorption energies are calculated by *ab initio* configuration interaction techniques modelling the surface as an embedded cluster. Adsorption energies of planar C_6H_6 at the most stable, 3-fold, adsorption site are 18 kcal/mol for the Ni(111) surface, and 10, 19, and 44 kcal/mol in the presence of the Na, H, and C interstitials, respectively. The energies required for the planar to puckered distortion are 99 kcal/mol on Ni(111), 69 kcal/mol with the Na interstitial, 83 kcal/mol with H, and 134 kcal/mol with C compared to 198 kcal/mol for distortion of C_6H_6 in the gas phase. The possible relevance of these results to the nucleation of diamond on nickel are discussed. The results indicate that subsurface Na stabilizes tetrahedrally bonded carbon subunits of the diamond structure while subsurface C may make it easier for the overlayer to revert to a planar graphite structure.

6. Theoretical Studies of Surface Reactions: Embedded Cluster Theory

J. L. Whitten, Chem. Phys., **177**, 387 (1993).

Abstract: A theoretical approach to the description of the electronic structure of molecules adsorbed on solid surfaces and surface reactions is described. The objective is a quantitative, molecular level, understanding of surface processes, including chemisorption energetics, adsorbate structure and reaction mechanisms. The electronic structure problem is formulated as an embedded cluster of atoms in which a localization transformation is used to define the electronic subspace that interacts strongly with the adsorbate and surface region. This permits *ab initio* SCF and CI calculations of molecular quality to be performed on a portion of the lattice-adsorbate system. Assumptions of the theory are discussed and applications to chemisorption on transition metal substrates are referenced.

7. Chemical Modification of Surface Steps on Si(111) vicinal Wafers: A Bonding Model for Phase Changes in Second Harmonic Generation Contributions to Silicon-Hydrogen Bond-Stretching Frequency in Amorphous Alloys

Z. Jing, J. L. Whitten and G. Lucovsky, Mat. Res. Soc. Symp. Proc., **313**, 287, (1994).

Abstract: There have been several studies of second harmonic generation (SHG) from chemically-modified vicinal Si(111) wafers. The SH fields contain one-fold and three-fold symmetry contributions, which originate respectively from the terrace and surface step atoms. The phase of these contributions are different for native oxides, and are a function of the frequency of the incident radiation. To identify the origin of these different phases for the terrace and step SH fields, we use a classical anharmonic oscillator model based on two assumptions: (a) a significant fraction of Si atoms at the steps have dangling bonds when oxides are formed below ~850C, and (b) these step atoms are linked to atoms at the bottom of the steps by O-Si-O groups following annealing at >900C.

8. Pathway of H₂ Desorption from Dihydride Si(100)

Ze Jing and J. L. Whitten, Phys. Rev. **B48**, 17296 (1993).

Abstract. In the present paper, the pathway of H₂ desorption from a dihydride species -SiH₂ on the Si(100) surface, -SiH₂ ----> -Si + H₂ (-Si represents a surface Si atom site), is investigated. This pathway involves the recombination of two H atoms bonded to the same surface silicon atom. A three-layer cluster which consists of 12 silicon atoms and 20 hydrogen saturators is used to simulate the Si(100) surface and *ab initio* SCF and CI theory is used to treat the cluster and desorption reactions. With the correction of zero-point vibrational energies, the H₂ desorption energy and activation barrier are computed to be 48 kcal/mol and 53 kcal/mol, respectively. The corresponding adsorption barrier is 5 kcal/mol. Considering the experimental uncertainty and the uncertainty of our calculations, we conclude that the barrier of H₂ desorption from the dihydride surface via -SiH₂ is consistent with the experimental result.

9. Bonding of Carbon to Nickel Surfaces: Effect of Subsurface Na, H and C

H. Yang, J. L. Whitten and R. J. Markunas, *Applied Surface Science* **75**, 12 (1994).

Abstract: This paper reports the results of a theoretical study of Na, H and C subsurface atomic species in nickel and demonstrates how these interstitial atoms influence the

reactivity of the Ni(111) surface and the structure of carbon species adsorbed on the surface. The CH_3 fragment and the benzene molecule, C_6H_6 , in planar and nonplanar geometries, are used to probe bonding at the surface. Adsorption energies are calculated by *ab initio* configuration interaction techniques modeling the surface as an embedded cluster. Calculated chemisorption energies of pyramidal CH_3 on Ni(111) are 38 for the clean surface and 50, 47, and 17 kcal/mol for the Na, H, and C implants, respectively. The energies required to distort tetrahedral CH_3 into a planar structure are 22 kcal/mol on clean Ni(111), 30 kcal/mol with the Na implant, 24 kcal/mol with the H implant and 12 kcal/mol with the C implant, respectively. Adsorption energies of planar C_6H_6 at the most stable, 3-fold, adsorption site are 18 kcal/mol for the Ni(111) surface, and 10, 19, and 44 kcal/mol in the presence of the Na, H, and C interstitials, respectively. The energies required for the planar to puckered distortion are 99 kcal/mol on Ni(111), 69 kcal/mol with the Na interstitial, 83 kcal/mol with H and 134 kcal/mol with C, compared to 198 kcal/mol for distortion of C_6H_6 in the gas phase. The possible relevance of these results to the nucleation of diamond on nickel are discussed. The results indicate that subsurface Na stabilizes tetrahedrally bonded carbon subunits of the diamond structure while subsurface C may make it easier for the overlayer to revert to a planar graphite structure.

10. Effects of Oxygen on Surface Reconstruction of Carbon

J. L. Whitten, P. Cremaschi and R. J. Markunas, *Applied Surf. Sci.*, **75**, 45 (1994).

Recent experiments on diamond growth by chemical vapor deposition indicate that atomic oxygen converts the diamond (100)-(2x1) surface to the (1x1) structure. *Ab initio* total energy calculations are performed on a cluster of carbon atoms simulating the (100) surface in order to investigate the effect of oxygen on surface reconstruction. Calculations are reported for the clean surface and for O atoms adsorbed atop carbon and at a C - C bridge site. Bridge and atop carbon sites for oxygen have nearly identical adsorption energies and adsorption of O at either site prevents the C(100)-1x1 to 2x1 dimerization reconstruction. Adsorption of oxygen at one bridge site is also found to inhibit the dimerization reconstruction of an adjacent pair of surface carbon atoms.

11. Theoretical Studies of Si-O and Si-N Bonding Arrangements on Vicinal Si(111) Wafers

Z. Jing, G. Lucovsky and J. L. Whitten, *Phys. Rev. B* **49**, 14003 (1994).

Abstract. The bonding at O (N) atom terminated dangling bonds at steps in the 112 direction is investigated by *ab initio* cluster calculations. We find that one Si atom, and three O (N) atoms, i.e., an SiO_3 (SiN_3) group, can bridge three dangling bonds such that the strain induced at the step by these bonding groups is negligible. The results help to explain the significant changes in the interface trap density, D_{it} , and the relative phase of the one-fold and three-fold contributions to the SHG from oxide terminated vicinal Si surfaces formed by thermal oxidation at 850°C following annealing at temperatures ~1000°C, where Si-O atom arrangements can readily occur.

12. *Ab Initio* Studies of H Chemisorption on C(100) Surface

Ze Jing and J. L. Whitten, *Surface Science*, **314**, 300 (1994).

Abstract: *Ab initio* CI theory is used to study the chemisorption of hydrogen on the C(100) surface. A three-layer cluster which consists of 19 carbon atoms and 30 hydrogen saturators is used to simulate the major features of surface reconstruction. The chemisorption of H atoms changes the surface reconstruction, shifting the dimer length from 1.51 Å in an H-free surface to 1.68 Å and 1.70 Å for a dimer bonded with one and two H atoms, respectively. The C-H bond energy is calculated to be 3.87 eV for the chemisorption of the first H atom and 4.14 eV for the chemisorption of the second H atom, including the corrections of zero-point vibrational energies. The C-C dimer bond energy in the monohydride phase is computed to be 1.21 eV. In forming the dihydride phase, the chemisorption of additional H atoms destroys surface dimers and changes the reconstructed 2x1 surface to a structure for which the interactions between surface CH₂ groups are repulsive.

13. Reaction of CH₄ and CH₃F with Si(111)

H. Yang, Z. Jing and J. L. Whitten, *J. Electron Spectrosc. Phenom.* **69**, 23 (1994).

Abstract: *Ab initio* configuration interaction theory coupled with cluster model calculations is used to study the reactions of CH₄ and CH₃F on a Si(111) surface. The lattice is modeled as a three layer cluster of 13 Si atoms plus 27 H atoms. The calculated heat of reaction for CH₄ + Si(111) → CH₃ + H-Si(111) is endothermic by 13 kcal/mol, with an energy barrier of 24 kcal/mol. The reaction CH₃F + Si(111) → CH₂F + H-Si(111) is calculated to be 12 kcal/mol endothermic, with an energy barrier of 20 kcal/mol. The reaction CH₃F + Si(111) → CH₃ + F-Si(111) is calculated to be 24 kcal/mol exothermic, with an energy barrier of 19 kcal/mol. F, H, CH₃, and CH₂F species are found to bind very strongly to the Si(111) surface, with adsorption energies of 132, 86, 78, and 76 kcal/mol, respectively. Equilibrium geometries, vibrational frequencies and transition state geometries for the transfer of H and F in reactions of CH₄ and CH₃F with Si(111) are reported.

14. Chemisorption Studies of CH₃S on Ni(111)

H. Yang, T. C. Caves, J. L. Whitten and D. R. Huntley, *J. Am. Chem. Soc.*, **116**, 8200 (1994).

Abstract: The chemisorption of methyl thiolate on Ni(111) is treated using a many-electron embedding theory, modeling the lattice as a 28-atom, three layer cluster with the Ni atoms fixed at the positions from the bulk. Methyl thiolate binds strongly to the Ni(111) surface at both high and low symmetry sites. Calculated adsorption energies are 61 kcal/mol for an equilibrium sulfur-surface distance of 1.99 Å at three-fold sites, 61 kcal/mol with a sulfur-surface distance of 2.06 Å at bridge sites, and 57 kcal/mol with a sulfur-surface distance of 2.13 Å at atop sites. Different equilibrium geometries are predicted for CH₃S at three-fold, bridge, and atop sites. The methyl thiolate C-S axis is nearly perpendicular to the surface, inclined only about 5° from the surface normal, at the three-fold site. The C-S axis is found to be tilted away from the surface normal by 45° at the bridge site, and by 55° at the atop site. For the C-S axis perpendicular to the surface,

the calculated C-S stretching vibration is 730 cm^{-1} , and the CH S-surface stretch is 281 cm^{-1} at the three-fold site. For a 45° tilt at the bridge site and a 55° tilt at the atop site, the C-S stretching vibrations are 677 cm^{-1} and 698 cm^{-1} , respectively.

15. Adsorption of CH_3O on Ni(111)

H. Yang, J. L. Whitten and C. M. Friend, Surface Science 313, 295 (1994).

Abstract: The adsorption of methoxy on Ni(111) is treated using a many-electron embedding theory, modeling the lattice as a 28-atom, three layer cluster. *Ab initio* valence orbital configuration interaction (multiple parent) calculations carried out on a local surface region permit an accurate description of bonding at the surface. The 3d orbitals are explicitly used for four Ni atoms in the local surface region. Methoxy binds strongly to the Ni(111) surface at both three-fold and bridge sites with adsorption energies of 90 and 87 kcal/mol and O-surface distances of 1.51 and 1.59 Å, respectively. The calculated adsorption energy for methoxy at an atop Ni site is 61 kcal/mol with an O-surface distance of 1.82 Å. The methoxy C-O axis is normal to the surface or inclined 5° or 10° from the surface normal at three-fold sites, and is inclined 20° from the surface normal at bridge sites. For methoxy adsorbed at three-fold and bridge sites, the calculated C-O stretching frequencies are 1025 and 1010 cm^{-1} , and CH_3O -surface perpendicular stretching frequencies are 495 and 380 cm^{-1} , respectively. The $5a_1$, $1e$ and $2e$ orbitals of adsorbed methoxy are the orbitals principally involved in bonding with the surface. The bonding of methoxy to the nickel surface is characterized as a combination of ionic and covalent bonding with substantial mixing with Ni 3d orbitals. Adsorption studies of $\text{CH}_3\text{O-Ni}$ and $\text{CH}_3\text{O-Ni}_3$ are also reported. Methoxy basis effects and bonding properties of methoxy upon adsorption on Ni are discussed.

16. Second Harmonic Response of Chemically Modified Vicinal Si(111) Surfaces

U. Emmerichs, C. Meyer, H. Bakker, H. Kurz, C. H. Bjorkman, C. E. Shearon, Jr. Y. Ma, T. Yasuda, Z. Jing, G. Lucovsky and J. L. Whitten, Phys. Rev., B50, 5506 (1994).

Abstract: We have studied the optical second-harmonic (SH) response of vicinal Si(111) interfaces, H-terminated or covered with a thermally grown oxide film and subjected to different annealing temperatures. We observed that the rotational anisotropy of the SH signal of a thermally grown oxide film changes after an annealing procedure. We explain this result from a modification of atomic bonding at the steps of the surface. The change in amplitude and phase of the nonlinear-optical response can be well described with an anharmonic oscillator model. We found that the nonlinear-optical signal can be correlated with the electrical quality (density of interface traps) of metal-oxide semiconductor devices produced from these Si/SiO₂ structures.

17. Theoretical Studies of C(100) Surface Reconstruction and Reaction with CH_2

Z. Jing, and J. L. Whitten, Mat. Res. Soc. Symp. Proc., 339, 54, (1994).

Abstract: The reconstruction of the C(100) surface and its reaction with CH_2 are studied by a cluster model at several theoretical levels [1-13]. For the reconstruction of the C(100)

surface, the calculated surface dimer bond length is found to be very sensitive to the level of theoretical treatment and the spin state. A single-determinant SCF treatment gives a closed-shell singlet state, higher in energy than the triplet state, and with a dimer length of 1.401 Å, 0.279 Å shorter than the triplet. The correct ground state is a singlet, but a multi-determinant wavefunction is required for its description. At the CI level, the surface dimer bond length in the ground state is found to be 1.508 Å and the energy decrease on dimer formation with respect to the ideal C(100)-1x1 surface is 2.28 eV per dimer. For the reaction of CH₂ with C(100), no barrier is found for the chemisorption of CH₂ on the surface and the reaction is highly exothermic. The surface is converted from C(100)-2x1 to C(100)-1x1 upon CH₂ chemisorption.

18. Nitrogen: Not a Dopant in Crystalline Si (c-Si), But an N-type Dopant in a-Si:H, Why?

G. Lucovsky, M. J. Williams, S. S. He, S. M. Cho, Z. Jing, and J. L. Whitten, Mat. Res. Soc. Symp. Proc., **336**, 637, (1994).

Abstract: We have incorporated N-atoms into hydrogenated amorphous silicon in the Si-rich alloy regime to ~12 at.% N, and have observed a transition from n-type doping to alloying as the concentration of N-atoms is increased above about 5 at.%. By analogy with the local bonding arrangements of P-donors in n-doped a-Si:H, we attribute the doping to four-fold coordinated N-atoms with second neighbor H-atoms as in N⁺-Si-H linkages. The occurrence of these arrangements is supported by (I) IR studies which indicate a non-statistical association of N and H-atoms bonded to the same fold coordinated N⁺ atoms and neutral O-atoms promote similar bonding properties with respect to their nearest-neighbor arrangements with Si and H atoms such as N⁺(O)-Si-H linkages.

19. New Model for Local H-atom Bonding Re-arrangements Associated with the Staebler-Wronski Effect in a-Si:H and a-Si:H-Based Alloys

G. Lucovsky, M.J.Williams, S.M.Cho, Z. Jing and J. L. Whitten, Mat. Res. Soc. Symp. Proc., **336**, 275, (1994).

Abstract: Many photoelectronic properties of a-Si, N:H alloys prepared by remote PECVD (RPECVD) from two N-atom source gases - N₂ and NH₃ - are the same; however, the photo-induced changes in the electrical properties in alloys with ~ 2.1 eV bandgaps are ~3 to 5 times greater in alloys deposited from NH₃, which display Si-NH, as well as SiH bonding. Based on this result, we show that bonding groups important in the Staebler-Wronski effect include -SiH, and nearest-neighbor -Si-NH-Si- and/or - Si-O-Si- in which the respective N and O-atoms make H-bonds with the -SiH group. The model, based on *ab initio* calculations, involves a H-exchange reaction in which trapping of photo-generated holes promotes a transfer of the H-atom from the -SiH group to a nearest-neighbor -Si-NH-Si creating a Si-dangling bond and a metastable (-Si-NH₂-Si)+ group. Calculations indicate that neutral (-Si-NH₂-Si-) is unstable, so that relaxation of (-SiNH₂-Si)+ groups can occur by trapping of a thermally released (trapped) electron during a post-light-soaking thermal anneal. The same type of model is developed for hole/electron trapping-induced H-atom transfer between -SiH and -Si-O-Si- groups in other a-Si:H materials.

20. Optical Second Harmonic Generation: A Probe of the Local Atomic Structure and Bonding at Si-SiO₂ Interfaces, and Other Chemically-Modified Si Surfaces

G. Lucovsky, C. E. Bjorkman, T. Yasuda, Yi Ma, Z. Jing and J. L. Whitten, U. Emmerichs, C. Meyer, H. Bakker, K. Leo, H. Kurz, J. Vac. Soc. Technol., **B12**, 2484 (1994).

Abstract: Optical second harmonic generation (SHG) is a highly surface-sensitive probe for studying crystalline Si surfaces because the inversion symmetry is broken and electric dipole optical SHG processes forbidden in the bulk are allowed. The polarized optical SHG from a perfectly-oriented Si surface is inherently anisotropic, varying periodically as the in-surface projection of the polarization vector of the incident laser is rotated about a normal to the surface. The harmonic contributions to the angular anisotropy are characteristic of the surface-bonding, and are modified by misorientation, chemical termination, as well as thermal treatment. Studies on Si(111) wafers with misorientations of 0° to 5° in the [112] direction are presented for Si-H or Si-O terminated surfaces. Azimuthal anisotropy data are compared with an empirical model for the SHG intensity that is based on the non-linear response of anharmonic oscillators, and includes a phenomenological theory of azimuthal anisotropies expected for different surface orientations. This model provides a framework for estimating resonance energies, thereby gaining insights into the microscopic mechanisms that contribute to the optical SHG. Correlations between SHG and electrical performance of the same Si-SiO₂ interfaces are discussed, and important differences between thermally-grown and plasma-oxidized interfaces are identified.

21. Ab Initio Studies of Diamond (100) Surface Reconstruction

Z. Jing and J.L. Whitten, Phys. Rev. **B50**, 2598, (1994).

Abstract: The reconstruction of the C(100) surface is studied by a cluster model at several theoretical levels. It is found that the calculated surface dimer bond length is very sensitive to the level of theoretical treatment, the spin state and the degree of constraints in the geometry optimization process. A single-determinant SCF treatment gives a closed-shell singlet state, higher in energy than the triplet state, and with a dimer length of 1.401 Å, 0.279 Å shorter than the triplet. The dimer is found to be symmetric for both singlet and triplet states at the SCF and CAS(2,2) levels of theory. The correct ground state is a singlet, but a multi-determinant wavefunction is required for its description. At the CI level, the surface dimer bond length in the ground state is found to be 1.508 Å and the energy decrease on dimer formation with respect to the ideal C(100) 1x1 surface is 2.28 eV per dimer.

22. Adsorption of Formyl on Ni(100)

H. Yang and J. L. Whitten, Langmuir, **11**, 853 (1995).

Abstract: The adsorption of formyl radicals (HCO) on Ni(100) is treated using a many-electron embedding theory, modeling the lattice as a 30-atom, three layer cluster with the Ni atoms fixed at bulk. *Ab initio* valence orbital configuration interaction (multiple parent) calculations carried out on a local surface region permit an accurate description of bonding at the surface. The 3d orbitals are explicitly used for six Ni atoms in the local

surface region. The Ni(100) potential surface is very flat for η^1 -formyl-C adsorption. η^1 -formyl-C binds to the surface mainly via the C atom, and the energy minimum occurs for an O-C-surface normal angle of 90° , 90° , and 110° at four-fold, bridge, and atop sites, respectively. The HCO bond angle is 120° . Calculated adsorption energies are 63.7, 63.5, and 63.6 kcal/mol at four-fold, bridge, and atop sites, with C-surface distances of 1.93 Å, 1.94 Å, and 2.04 Å, respectively. Calculated C-O stretching frequencies are around 1760 cm^{-1} and C-H stretching frequencies are around 2940 cm^{-1} for HCO at all adsorption sites and equilibrium geometries. The bonding of formyl to the nickel surface involves ionic and covalent contributions and substantial mixing with Ni 3d orbitals. Calculated η^1 -formyl-O, bonding to the surface via the O atom, is energetically less stable than η^1 -formyl-C by 16.3 kcal/mol. Calculated C-O and C-H stretching frequencies are 1370 cm^{-1} and 2988 cm^{-1} for η^1 -formyl-O at four-fold sites. No energy barrier occurs for the conversion of η^1 -formyl-O to η^1 -formyl-C.

23. Embedded Cluster Theory: Reactions on Metal and Semiconductor Surfaces

J. L. Whitten, chapter in "Electronic Properties of Solids using Cluster Methods," Eds. T. A. Kaplan and S. D. Mahanti, Plenum Press, New York, 1995, p 53-62.

24. *Ab Initio* Chemisorption Studies of H on Fe(110)

P. Cremaschi, H. Yang and J. L. Whitten, Surface Science, **330**, 255 (1995).

Abstract: *Ab initio* configuration interaction calculations are performed to study the chemisorption of atomic H on a Fe(110) surface. The lattice is modeled as an embedded three-layer, 40-atom cluster with the Fe atoms fixed at the bulk position. Fe 3d orbitals are explicitly included on five Fe atoms on the surface. Hydrogen strongly binds to the Fe(110) surface at the long-bridge, short bridge, and quasi three-fold sites. The calculated adsorption energies are 2.76, 2.73, and 2.71 eV, respectively. H-surface bonding at the on-top Fe site is more than 0.4 eV weaker. The calculated H-surface distances are 0.89 Å, 1.03 Å, and 0.87 Å for H at the long-bridge, short-bridge, and quasi three-fold sites, respectively, which agrees well with the LEED value of 0.9 ± 0.1 Å. The H-surface stretching vibrational frequencies are calculated to be 1070, 1066, and 1073 cm^{-1} , at the long-bridge, short-bridge, and quasi three-fold sites, respectively. The work function of Fe(110) decreases on H adsorption. The present calculations indicate that H diffusion into the bulk through the short-bridge site will have a much higher activation barrier than via the long-bridge and quasi three-fold sites.

25. Multi-Configuration Self-Consistent-Field treatment of H_2 desorption from Si(100)-2x1H

Ze Jing and Jerry L. Whitten, J. Chem. Phys., accepted, (1995).

Abstract: The present work studies the symmetric and asymmetric pathways of the recombinative desorption of molecular hydrogen from the monohydride Si(100)-2x1H surface by the cluster method. The transition states are searched at the self-consistent-field and multi-configuration self-consistent-field levels of theory and the energies are calculated at the configuration interaction level of theory. For the asymmetric transition state, the

structure determined at the self-consistent-field level is similar to that determined at the multi-configuration self-consistent-field level. However, for the symmetric transition state, electron correlation is found to play such a crucial role that multi-configuration self-consistent-field has to be used to obtain the saddle point. At the configuration interaction level of theory, the activation energies for the symmetric and asymmetric pathways are computed to be 86.3 and 85.0 kcal/mol, respectively. Compared with the experimental values of 45-66 kcal/mol, the large barriers suggest that the direct desorption mechanism is not applicable. A multi-step desorption mechanism which involves a delocalized process in the formation of dihydride SiH_2 and a localized desorption of H_2 has been proposed to explain the experimental observations.

26. Hydrogen Bonding Arrangements at Si-SiO₂ Interfaces

Z. Jing, G. Lucovsky, and J. L. Whitten, J. Vac. Soc. Technol., **B13**, 1613 (1995).

Abstract: An important issue in semiconductor device operation is the rate at which current or voltage stress creates defects that degrade eventually device operation. Based on recent results on nitrided gate dielectrics, we have concluded that bonded-H at the Si-SiO₂ interface plays a role in the formation of metastable defects that can be activated, and subsequently neutralized, by sequential trapping of injected holes and electrons. In this paper, differences in defect behavior for Si-SiO₂ interfaces that have exposed to nitrogen (N-) atoms or N-H groups are discussed. Based on these results, a microscopic model for interfacial defects is proposed.

27. *Ab Initio* Studies of CN Adsorbed on Ni(111)

H. Yang, T. C. Caves, and J. L. Whitten, J. Chem. Phys. 103 (1995) 8756.

Abstract: The adsorption of cyanide (CN) on Ni(111) is treated using an *ab initio* embedding theory. The Ni(111) surface is modeled as a three-layer, 28-atom cluster with the Ni atoms fixed at bulk lattice sites. The present calculations show that CN is able to bind to the surface either via the carbon, or nitrogen, or in a side-on geometry with very small differences in total energy (≈ 0.1 eV). Adsorption energies at three-fold, bridge and atop sites are comparable, with the fcc three-fold site more favorable over other adsorption sites by ≈ 0.1 eV. At the fcc three-fold site, adsorption energies and C-N stretching frequencies are 5.0 eV and 2150 cm^{-1} for the η^1 -cyanide-N, 4.9 eV and 1970 cm^{-1} for the η^1 -cyanide-C, and 4.9 eV and 1840 cm^{-1} for the η^2 -cyanide-C,N, respectively. Dipole moment calculations show that the bonding of CN to the Ni surface is largely ionic, while η^2 -cyanide-C,N has more covalent character. Calculated energy barriers in going from η^1 -cyanide-C to η^2 -cyanide-C,N, and from η^2 -cyanide-C,N to η^1 -cyanide-N are around 0.1 eV. Thus, although CN is strongly bound to the surface (at ≈ 5 eV), within an energy range of ≈ 0.2 eV, the molecule is free to rotate to other geometries. During this rotation there are large changes in the dipole moment

28. Metastable Defects at Si/SiO₂:H Interfaces

G. Lucovsky, Z. Jing and J. L. Whitten, J. Vac. Soc. Technol., accepted, (1995).

Abstract: Hydrogen is often intentionally introduced at Si-SiO₂ interfaces of MOSFET

devices to compensate Si-stom dangling bonds. What has not been recognized to date is that the H-atoms of interfacial Si-H groups can also form weaker bonds with O-atoms of the SiO₂ network, and thereby reduce device reliability. Specifically, H-atoms of interfacial Si-H groups will form weak bonds with electronegative species such as O-atoms and/or NH groups at Si-SiO₂ interfaces that subsequently act as precursor sites for charge trapping reactions leading to defect generation. Quantum chemistry calculations have revealed that trapping a hole at an O-atom that is coupled to an interfacial Si-H bond leads to the formation of a three-fold coordinated and positively-charged oxonium center in the dielectric (fixed positive charge, Q_f⁺) and a neutral dangling bond (D_{it} defect) at the Si-SiO₂ interface. Subsequent trapping of electron will return this molecular environment to its original state via a displacive motion of the H. Similar reactions also occur at NH sites, wherein the over-coordinated group is an ammonium center (Si₂NH₄⁺). For these interfacial O and NH-species, *ab-initio*-based reaction equations demonstrate that the defect metastability is driven simply by charged carrier quantum chemistry approach shows that this type of behavior is not possible at interfacial N-atom sites wherein the three nearest neighbors to the N-atom are Si. The implications of these calculations for interfacial device engineering are discussed, and have been validated by experiments wherein interfacial N-atoms and NH-groups introduced at Si-SiO₂ interfaces have yielded different defect behaviors.

29. Properties of Bonded Hydrogen in Hydrogenated Amorphous Silicon and Other Hydrogenated Amorphous Silicon Alloys

G. Lucovsky, Z. Jing, S. Lu, D. R. Lee and J. L. Whitten, J. Non-Cryst. Solids, accepted, (1996).

30. Theoretical Studies of Surface Reactions on Metals

J. L. Whitten and H. Yang, Int. J. Quantum Chem.: Quantum Chemistry Symposium, 29, 41-47 (1995).

This paper describes a theoretical approach for treating chemisorption and surface reactions on metals. Electronic structures are described by an *ab initio* embedding formalism that permits an accurate determination of reaction energetics and adsorbate structure.

Chemisorption energies, adsorbate structures and the reaction of coadsorbed species are reported for methane thiolate on Ni(111) to illustrate the method.

31. Theoretical Adsorption Studies of HCN and HNC on Ni(111)

H. Yang and J. L. Whitten, J. Phys. Chem., 100, 5090 (1996).

Abstract: The interaction of hydrogen cyanide (HCN) and hydrogen isocyanide (HNC) with Ni(111) is studied using an *ab initio* embedding theory. The Ni(111) surface is modeled as a three-layer, 28-atom cluster with the Ni atoms fixed at bulk lattice sites. The present calculations show that both HCN and HNC bind to the surface in an end-on geometry with the molecular axis perpendicular to the surface. Tilting either the H atom or the H-C bond or the H-N bond away from the surface normal destabilizes the system. The side-on bonded HCN and HNC with the C-N bond parallel to the surface are energetically

less stable than the corresponding end-on bonded species. The calculated adsorption energy of the end-on HCN is 18 kcal/mol with the fcc three-fold site favored over other sites by about 1 to 3 kcal/mol. The end-on HNC binds to the surface at the atop site with adsorption energy of 11 kcal/mol. The calculated adsorption energy for the side-on bonded HCN is only 7 kcal/mol. The side-on bonded HNC species is found to be unbound by 12 kcal/mol on Ni(111). Calculated C-N stretching frequencies are 2200 cm^{-1} and 2100 cm^{-1} for end-on bonded HCN and HNC, and 2105 cm^{-1} and 1530 cm^{-1} for the side-on bonded HCN and HNC, respectively. Dipole moment calculations show that the bonding of HCN to the surface is relatively more ionic than HNC.

32. Chemisorption of CNH_2 and HCNH on the Ni(111) Surface

H. Yang and J. L. Whitten, Chem. Phys. Lett., **251**, 20 (1996).

Abstract: The chemisorption of CNH_2 and HCNH on Ni(111) is studied using an *ab initio* configuration interaction embedding theory. Both CNH_2 and HCNH strongly bind to the Ni(111) surface with HCNH more stable by 31.7 kcal/mol. CNH_2 is adsorbed at a bridge site via the C atom. Both C and N atoms in HCNH are involved in bonding to the surface with the C-N bond parallel to the surface. The calculated C-N stretching frequencies and bond lengths are 1335 cm^{-1} and 1.32 Å for CNH_2 and 1457 cm^{-1} and 1.32 Å for HCNH , respectively..

33. Theory of Chemisorption and Reactions on Metals

J. L. Whitten and H. Yang, Surf. Sci. Reports, **218**, in press (1996).

Abstract: A review of theoretical methods used to describe chemisorption and adsorbate reactions on metal surfaces is contained in this report. A comprehensive perspective on state-of-the-art electronic structure methods suitable for these problems and a review of applications that illustrate current capabilities of theory are presented. First-principles *ab initio* and density functional methods and semiempirical approaches that permit the calculation of adsorbate energetics, structure and spectra are emphasized. In addition to the chemisorption of molecules and molecular fragments, applications include gas-surface reactions, dissociative processes and surface reactions involving coadsorbed species. Many of the applications are relevant to transition metal heterogeneous catalysis. Both slab and atomic cluster methods are described. Methods are critiqued, with reference to published applications, to illustrate capabilities and limitations of different approaches. An extensive compendium of applications is included.

34. *Ab Initio* Adsorption Studies of HCO on Ni(111)

H. Yang, Surf. Sci., **343**, 61 (1995).

Abstract: The adsorption of formyl (HCO) on Ni(111) is treated using an *ab initio* embedding theory. HCO, characterized as η^1 -formyl-C, binds strongly to the Ni(111) surface mainly via the carbon atom. Calculated adsorption energies are 59.4, 57.2, and 57.0 kcal/mol at atop, three-fold, and bridge sites, respectively. The minimum energy occurs for an O-C-surface normal angle of 90° and HCO bond angle of 120° at all sites. All calculated C-O stretching frequencies are around 1755 cm^{-1} and C-H stretching

frequencies are around 2970 cm^{-1} . Substantially mixing between Ni 3d orbitals with higher HCO orbitals occurs. η^1 -formyl-O is energetically less stable than η^1 -formyl-C by 18 kcal/mol.

35. Metastable, Electronically-active Defects Associated with H-bonds: Applications to Hydrogenated Amorphous Silicon, and Si-SiO₂ Interfaces

G. Lucovsky, Z. Jing, M.J. Williams, S.M. Cho, D.R. Lee and J.L. Whitten, submitted, (1996).

Abstract: Light-induced defects (LIDs) place significant constraints on the performance of hydrogenated amorphous silicon (a-Si:H) photovoltaic (PV) devices. Stress-bias induced defects at, or in the immediate vicinity of Si-SiO₂ interfaces place similar limitations on the performance, and the reliability of insulated-gate field effect transistors (FETs). This paper demonstrates how trapping of charged carriers at local atomic sites that include H-bonding arrangements can explain the observed defect creation, and defect metastability in both types of materials systems. Experimental evidence for the proposed model is based on changes in defect creation and metastability behavior that are correlated with the process-controlled introduction and/or elimination of specific chemical environments that are known to promote strong H-bonding interactions. The proposed model is supported by ab initio calculations of bond energies in the normal and metastable defect state configurations.

IV. Personnel Supported by DOE Grant

Postdoctoral Research Associate, Z. Jing

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Undergraduate student, no cost

Graduate student on fellowship (one year), no cost

Visiting scientist Dr. P. Cremaschi, no cost.

Principal investigator J. L. Whitten, 2 months per year