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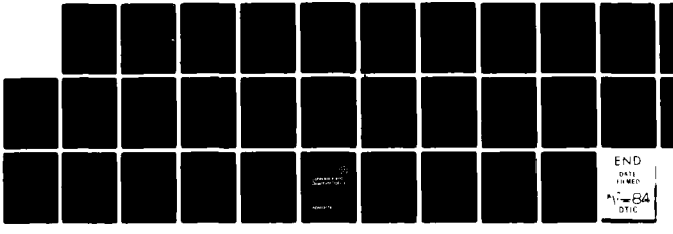

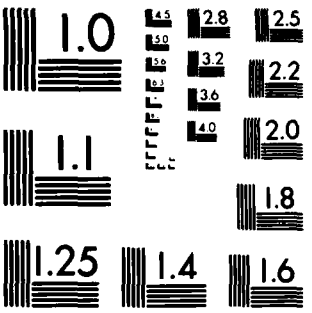

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Recent experiments have demonstrated that laser radiation incident on a gas-surface interface can stimulate and control the process of vapor deposition onto the surface. This research project has been a theoretical analysis of the deposition and related laser-stimulated processes, with special attention given to the microscopic dynamics of energy flow associated with such processes.

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THEORETICAL STUDY OF LASER-STIMULATED CHEMICAL VAPOR DEPOSITION PROCESSES OF IMPORTANCE IN MICROELECTRONICS

Final Report

Thomas F. George

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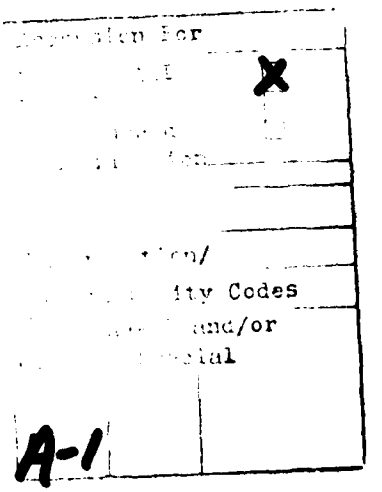

TABLE OF CONTENTS

I. MANUSCRIPTS PUBLISHED OR SUBMITTED UNDER ARO SPONSORSHIP

1. X. Y. Huang, J. Lin and T. F. George, "Model for the Propagation of Pulsed Surface Polaritons with Quasi-Self-Induced Transparency," Z. Phys. B 50, 181 (1983).

2. W. C. Murphy, A. C. Beri, T. F. George and J. Lin, "Analysis of Laser-Enhanced Adsorption/Desorption Processes on Semiconductor Surfaces via Electronic Surface State Excitation" in Laser Diagnostics and Photochemical Processing for Semiconductor Devices, ed. by R. M. Osgood, Jr. and S. R. J. Brueck (Elsevier, New York), Mat. Res. Soc. Symp. Proc. 17, 273 (1983).

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5. H. W. Lee and T. F. George, "Emission of Short-Wavelength Photons from Ion-Surface Charge Exchange," IEEE J. Quantum Electron., in press.

6. X. Y. Huang, J. Lin and T. F. George, "Resonance Fluorescence of a Two-Level Atom Near a Metal Surface," J. Chem. Phys., in press.

7. T. F. George, K. T. Lee, W. C. Murphy, M. Hutchinson and H. W. Lee, "Theory of Reactions at a Solid Surface" in The Theory of Chemical Reaction Dynamics, ed. by M. Baer (CRC, Boca Raton, Florida), in press.

8. T. F. George, J. Lin, A. C. Beri and W. C. Murphy, "Theory of Laser-Stimulated Surface Processes," Prog. Surf. Sci., in press.

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11. K. S. Lam, M. Hutchinson and T. F. George, "Laser-Induced Bound States at Surfaces: Ion Neutralization and Adsorption" in Collisions and Half-Collisions with Lasers, ed. by N. K. Rahman and C. Guidotti (Harwood Academic, Chur, Switzerland), in press.

12. K. C. Liu, K. S. Lam and T. F. George, "Localized Magnetization Arising from Spin-Dependent Potentials in the Wolff Model," Phys. Stat. Sol. (b), in press.

13. M. Hutchinson, K. T. Lee, W. C. Murphy, A. C. Beri and T. F. George, "Theoretical Aspects of Laser-Induced Periodic Surface Structure Formation" in Laser-Controlled Chemical Processing of Surfaces, ed. by A. W. Johnson and D. J. Ehrlich (Elsevier, New York), Mat. Res. Soc. Symp. Proc., in press.

14. X. Y. Huang, K. C. Liu and T. F. George, "Resonance Fluorescence and Photon Trapping of Two Atoms on a Metallic Surface" in Laser-Controlled Chemical Processing of Surfaces, ed. by A. W. Johnson and D. J. Ehrlich (Elsevier, New York), Mat. Res. Soc. Symp. Proc., in press.

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16. W. C. Murphy and T. F. George, "Laser-Induced Electron-Phonon Processes on Metal Surfaces," J. Chem. Phys., submitted.

17. X. Y. Huang and T. F. George, "Resonance Fluorescence of a Two-Level Atom Near a Metal Surface. II. Case of a Strong Driving Field," J. Phys. Chem., submitted.

18. I. Last, T. F. George and D. S. Perry, "Conductivity in Semiconductors Induced by Vibrational-to-Electronic Energy Transfer," J. Chem. Phys., submitted.

CONFERENCE ABSTRACTS

a. X. Y. Huang, T. F. George and J. Lin, "Resonance Fluorescence of a Two-Level Atom near a Metal Surface: Surface-Dressed Optical Bloch Equations," Abstracts of the Fifth Rochester Conference on Coherence and Quantum Optics (Rochester, New York, 1983), pp. 224-226.

b. H. W. Lee and T. F. George, "Emission of Short-Wavelength (XUV) Photons from Electron Capture by Ions at an Electronically-Excited Solid Surface," Abstracts of the Fifth Rochester Conference on Coherence and Quantum Optics (Rochester, New York, 1983), pp. 309-310.

c. A. C. Beri, W. C. Murphy, K. T. Lee, M. Hutchinson and T. F. George, "Microscopic Theory of Laser-Induced Periodic Surface Structure Formation," Final Program and Abstracts of the Materials Research Society 1983 Annual Meeting (Boston, Massachusetts, 1983), p. 409.

II. SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT

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Dr. Xi-Yi Huang, Research Associate

Dr. Michael Hutchinson, Research Associate

Dr. Kung C. Liu, Research Associate

Mr. Franco Battaglia, Graduate Student

III. STATEMENT OF THE PROBLEM STUDIED

Recent experiments have demonstrated that laser radiation incident on a gas-surface interface can stimulate and control the process of vapor deposition onto the surface. This research project has been a theoretical analysis of the deposition and related laser-stimulated processes, with special attention given to the microscopic dynamics of energy flow associated with such processes.

IV. SUMMARY OF THE MOST IMPORTANT RESULTS

A variety of basic phenomena contribute to the overall process of laser-stimulated chemical vapor deposition. One such phenomenon is the propagation of surface waves, particularly in connection with recently observed periodic structure in metal adsorbed on Si or SiO_2. As a step toward understanding this, we have combined the optical Bloch and Maxwell equations to describe the propagation of pulsed surface polaritons in a slab (two-interface) configuration, where one interface connects the gaseous medium with the deposited metal film and the other interface connects the film with the silicon substrate. A specific observation is that quasi-self-induced transparency, although seen in the case of a single interface, does not exist for the slab configuration. To look more specifically at the deposition process, we have used a perturbative solution of the Maxwell equations to study periodic deposition patterns on a relatively smooth surface grating, where the patterns result from an interference among the incident radiation, the reflected field and the surface plasmon field. As the surface grating is enhanced by the initial deposition, the perturbative solution breaks down, and alternate non-perturbative solutions have been developed for rough surfaces.

The role of laser-induced surface plasmons has also been investigated in connection with resonance fluorescence and migration. With respect to the first topic, surface-dressed optical Bloch equations, which include the surface-reflected field, have been used to calculate the population inversion and power scattering spectrum of a laser-driven two-level atom near a metal surface. Both the population inversion and power spectrum exhibit a strongly oscillatory behavior as a function of the atom-surface distance, such that resonance fluorescence is enhanced at certain distances and diminished at others due to the presence of the surface. With respect to the second topic, a classical model coupling a charged adspecies to a laser-induced surface plasmon has been developed. Such coupling can enhance the rate and specify the direction of surface migration. For the particular case of an atomic oxygen ion of charge -1 adsorbed on aluminum which is exposed to CO_2 laser radiation of intensity 1 W/cm^2, the velocity of migration (61.3 microns/sec) is five orders of magnitude greater than the usual thermal velocities observed at room temperature.

Focusing on the dynamical degrees of freedom of an adspecies-surface system, we have analyzed multiphonon effects on the vibrational excitation

of an adbond by an infrared laser. Using a generalized master equation, we have developed a computationally tractable description of a linear chain model. In regard to electronic degrees of freedom, we have considered the excitation of surface states in semiconductor and metal substrates. Such states are localized near the top of the surface, in contrast to bulk states (such as valence and conduction bands) which are properties of the entire substrate. The resulting effect of exciting surface states is an increased electronic charge at the surface. Calculations have been carried out for linear-chain models of silicon and sodium, where for the latter we must include electron-phonon coupling. It is demonstrated that deposition is enhanced when the positive end of a dipolar adspecies approaches the laser-excited semiconductor or metal.

This concept of surface-state excitation has been extended to include charge transfer processes in ion-surface collisions. For the cases of Li^{3+} ions, alpha particles and He^{+} ions colliding with Si(111), we have carried out semiclassical calculations of the probabilities of formation of the excited-state species Li^{2+}, He^{+} and He, respectively. It is shown that with a moderate-power laser (less than 10 W/cm^2) to excite surface states and hence enhance the charge transfer probabilities, high inversion densities can be obtained, as necessary for high gain. Although this aspect of the research does not deal directly with deposition, it does hold promise for establishing an efficient means of making XUV or X-ray lasers.

As a final topic, we have considered vibrational-to-electronic energy transfer at a semiconductor surface due to an impinging vibrationally-excited diatomic molecule. By promoting an electron to the conduction band, the transfer of a vibrational quantum leads to electron-hole pair formation. Probabilities around five percent have been calculated for the HCl + InSb and HCl + PbSe systems for thermal collision energies, which are large enough to be observed through measurements of the electrical conductivity.

V. TITLES AND ABSTRACTS OF MANUSCRIPTS

Z. Phys. B - Condensed Matter 50, 181-186 (1983)

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Model for the Propagation of Pulsed Surface Polaritons with Quasi-Self-Induced Transparency

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The possibility of quasi-self-induced transparency for the propagation of pulsed surface polaritons on a gas-solid interface is investigated. A theoretical model combining the optical Bloch and Maxwell equations is presented. The boundary conditions of the interface system lead to a closed relation between the laser pulse velocities in each of the two media. The behavior of transverse phase oscillations in hyperbolic secant pulses, due to the properties of the interface and the restriction of the pulse duration, are discussed. The treatment is extended to a slab (two-interface) configuration, where there is a restriction on the envelope of the pulsed slab mode such that quasi-self-induced transparency is no longer observed.

I. Introduction

The development of sources of pulsed coherent radiation (laser) has prompted investigations of the behavior of coherent traveling waves interacting with media which have absorption bands near or at the frequency of the applied pulse. Of particular interest are resonant absorbing media characterized by two-level transitions which are induced by optical radiation [1]. At the same time, increasing attention has been paid to the problem of surface polaritons (SP), which, in a simple case, occur at a single interface between two media, one having a negative dielectric (or magnetic) permeability and the other a positive one. The SP propagate along the interface and decay exponentially for directions normal to the interface [2]. Under usual conditions, due to radiation absorption or relaxation of the media, the SP propagating on the interface would decay rapidly, where the traveling distance for infrared SP are on the order of a cm [3].

It is established that an optical pulse propagating through an absorbing gas medium would be resonantly absorbed according to Beer's law when its intensity is low. As the intensity of the (coherent) laser radiation increases, the pulse may propagate through the absorber gas as if it were transparent. This phenomenon, called self-induced transparency, was predicted and demonstrated by McCall and Hahn [4, 5] and experimentally refined later [6].

In the present paper, we shall study an interface system comprised of a gas medium and a solid medium. In the next section we predict and present an analysis of quasi-self-induced transparency (quasi-SIT) for the propagation of SP on the interface of a two-level atomic gas and an unspecified "surface-active" medium, which is a solid material possessing a dielectric constant $\varepsilon_m(\omega)$ whose real part is negative near the frequency ω of interest. The term "quasi" is used as a prefix to SIT since there is decay in the solid medium through the imaginary part of ε_m. For the gas medium, the imaginary part of ε_g plays a negligible role in the saturated propagation governed by the nonlinear Bloch and Maxwell equations, so that the propagation is lossless. The relation between the laser pulse velocities in each media, which must match at the interface, and phase oscillations associated with hyperbolic secant pulses are revealed. In Sect. III the treatment is extended to a slab (two-interface) configuration, where there is a restriction on the envelope of the pulsed slab mode whereby quasi-SIT is no longer seen. Section IV contains some final remarks.

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ANALYSIS OF LASER-ENHANCED ADSORPTION/DESORPTION PROCESSES ON SEMICONDUCTOR SURFACES VIA ELECTRONIC SURFACE STATE EXCITATION

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ABSTRACT

Electronic surface states in semiconductors often lie between the valence and conduction bands and give rise to charge densities confined to the surface region. Laser radiation of frequency less than the energy gap can excite electrons from delocalized valence band states to these localized surface states leading to large changes in the charge distribution at the surface. Selective enhancement of adsorption/desorption processes involving ionic or polar adspecies can result from such a charge redistribution. Using a one-dimensional model for silicon, the cross-section for the laser-induced electronic transition to surface states is shown to be large. The interaction energy of an adspecies with the surface changes significantly with direct excitation of surface states in a semiconductor. For a one-dimensional metal, however, direct transitions between bulk and surface states are not allowed, but phonon-mediated transitions coupled with laser radiation lead to substantial charge transfer as for semiconductors.

INTRODUCTION

Much effort has been devoted to the study of the effects of laser radiation on the phonons in solid surfaces. Both theoretical [1] and experimental [2] works have relied on the laser to excite these vibrational modes of the system in order to enhance surface processes.

On the other hand, photo-induced surface reactions can occur through electronic excitation. Synchrotron radiation studies [3] on metal surfaces have shown induced desorption due to the shift of electronic charge in the surface region [4].

For a semiconductor, states with charge localized in the surface region exist in addition to the bulk conduction and valence bands states [5]. In the following, we will demonstrate the use of a laser for exciting charge into these surface states and discuss the effect on surface processes.

For a truncated one-dimensional chain of length L and lattice constant a, the solutions of the Schrödinger equation can be obtained within the nearly-free-electron approximation [5]. The energy for the bulk electronic states is

$$E_k = \frac{1}{4}\{[k^2+(k-g)^2] \pm \sqrt{[k^2-(k-g)^2]^2 + 4E_g^2}\} \qquad (1)$$

where k is the wavenumber of the electron, $g = 2\pi/a$ is the reciprocal lattice vector and E_g is the band gap energy. The results for the valence band (negative branch) and conduction band (positive branch) are illustrated in figure 1. The wavefunctions are constructed from sums of plane waves [6]. For

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Quantum-statistical theory of laser-stimulated surface processes. II. Nonequilibrium rate of laser excitation and multiphonon relaxation

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By means of quantum-statistical theory, the laser excitation rate and multiphonon relaxation rate are calculated for species adsorbed on cold and heated surfaces. The complex frequency of Bose operators is derived from a microscopic Hamiltonian with anharmonic mode-mode coupling, which provides the origin of the non-Arrhenius form for the multiphonon relaxation rate. The energy-transfer rate due to the interference effects between the coherent laser excitation and multiphonon coupling is calculated. The nonequilibrium energy-transfer rate due to the energy feedback of the heated surface is investigated via a self-consistent heat-diffusion equation.

I. INTRODUCTION

Laser-stimulated surface processes (LSSP), motivated by their potential importance in industrial applications and basic research in many areas, e.g., surface chemistry, materials science, and microelectronic processing, are receiving increasing attention. LSSP may be grouped into the selective type, e.g., excitation of a specific active mode, adspecies or migrational site,[1,2] and the nonselective type in which the laser radiation energy is transformed into heat.[3] These selective and nonselective aspects of LSSP are characterized not only by the pumping rate, as compared to the multiphonon relaxation rate, but also by the synergistic effects of the coherent laser pumping and the thermal phonon-induced excitation.[4]

Energy-transfer processes, resulting from laser excitation of an adspecies with consequent multiphonon relaxation, may be described by the rate equation for the active-mode excitation n_A,[5]

$$\dot{n}_A(t)=W_L-W_R[n_A(t)-\bar{n}_B]\,, \tag{1}$$

where W_L and W_R are the laser-excitation and phonon-induced relaxation rate, respectively, of the active-mode excitation, whose equilibrium value $\bar{n}_B$ is given by a Bose-Einstein distribution. The above rate equation can be derived from a microscopic Hamiltonian, where the Markovian approximation is assumed such that the "feedback" energy from the heated surface, characterized by the temperature-dependent bath-mode occupation number $\bar{n}_B(T(t))$, is completely eliminated, i.e., equilibrium statistics is used to treat the laser-induced transient phenomena. Furthermore, a constant multiphonon relaxation rate W_R is assumed in the rate equation.

Energy-transfer processes may also be depicted by a master equation,[2,4]

$$\dot{P}_n=\sum_m(W_{mn}P_m-W_{nm}P_n)\,, \tag{2}$$

where P_n is the energy population of state n, and W_{mn} is a total transition rate for a transition from m to n. This rate, induced by both the coherent laser field and the multiphonon relaxation, cannot, in general, be separated into the sum $W_{mn}(\text{total})=W_{mn}(\text{laser})+W_{mn}(\text{phonon})$, particularly for the situation of strong phonon coupling and/or high-power laser-excitation processes. Furthermore, the excitation of the phonon modes can result in a hot surface in which the feedback energy of the thermal phonons significantly affects the overall transition rate.

Here we shall develop a quantum-statistical theory for the total transition rate which includes the interference effects between the coherent laser field and the incoherent multiphonon coupling. In Sec. II a microscopic Hamiltonian including the anharmonic mode-mode coupling which provides the origin of a non-Arrhenius transition rate is investigated. The equilibrium transition rate for a cold surface and the nonequilibrium transition rate for a heated surface with energy feedback effects are

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QUANTUM DYNAMICAL MODEL FOR LASER EXCITATION OF A TWO-LEVEL ADATOM: SURFACE-DRESSED BLOCH EQUATIONS

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Surface-dressed Bloch equations are derived from a microscopic Hamiltonian which includes the interactions among an adatom, the laser photon and the phonon modes. The influence of the surface on the population inversion of the adatom is analyzed in terms of: (1) the reflected-field-induced damping factor which depends on the orientation of the transition dipole and the adatom-surface separation and (2) the frequency shift and damping factor induced by the phonon modes.

1. INTRODUCTION

THE INTERACTION of laser radiation with matter in homogeneous systems has been extensively studied for the past several years [1, 2]. However, for heterogeneous systems (e.g., gaseous atoms near or adsorbed on a solid surface) the laser-stimulated surface phenomena (desorption, dissociation, migration and reactions) involving both multiphoton and multiphonon processes have been only recently attacked [3–5]. In previous studies, we have investigated the excitation and relaxation dynamics of adspecies subjected to i.r. radiation in which only the vibrational degrees of freedom are concerned [4]. In the present paper, we shall investigate the electronic excitation of a two-level atom adsorbed on a metal surface and subjected to u.v. or visible laser radiation. In the absence of a solid surface or when the atom is very far from the surface, the population inversion and the power spectrum of the system may be described by an ordinary optical Bloch equation (OBE). In the presence of a surface at a distance from the adatom which is comparable to the optical wavelength, the dynamical phenomena are influenced by the following factors: (1) nonradiative energy relaxation of the excited atom via electron-phonon coupling; (2) radiative spontaneous decay and stimulated emission produced by both the applied field and the reflected field; (3) the oscillatory behavior of the lifetime of the adatom due to the interference between the applied field and the reflected field; (4) the reflectivity and refraction index of the surface; (5) surface-induced dephasing of the dipole; and (6) interaction between the adatom and plasmons; as a first step, we assume that the effects of the conduction electrons in the metal just provide a reflected field acting back to the adatom.

2. MICROSCOPIC HAMILTONIAN AND SURFACE-DRESSED BLOCH EQUATIONS

To investigate the above surface phenomena, we start with a microscopic Hamiltonian describing a two-level adatom subjected to laser radiation,

$$H = H_A + H_B + H_F + H_{AB} + H_{AF} + H_{AR} + H_{BF} \quad (1)$$

H_A, H_B and H_F are the unperturbed Hamiltonians for the adatom, phonon and photon (laser) modes, respectively; H_{AB}, H_{AF} and H_{AR} describe the interaction of the adatom (A) with the phonon bath (B) modes, the applied field phonon (F) modes and the reflected field (R), respectively; and H_{BF} is the interaction between the B modes and the applied field. For a laser frequency in the visible to u.v. range, the phonon (B) modes have much weaker absorption compared to that of the adatom, and thereby the direct heating of the substrate due to H_{BF} is negligible. In this work, the effect of H_{BF} will be displayed in terms of the strength of the reflected electric field due to the reflectivity of the surface.

Employing Pauli's matrices for the two-level adatom and harmonic ladder operators for the photon and phonon modes, the total Hamiltonian may be expressed

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EMISSION OF SHORT-WAVELENGTH PHOTONS FROM ION-SURFACE CHARGE EXCHANGE

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Abstract

The intensity of radiation emitted from ion-surface charge-exchange processes can be significantly enhanced if the surface exposed to impinging ions is electronically excited. Alpha particles capturing electrons at a silicon surface are considered as a possible candidate for a short-wavelength laser.

Resonance fluorescence of a two-level atom near a metal surface

J. Chem. Phys., in press.

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A derivation of surface-dressed optical Bloch equations, involving a treatment of surface-reflected photons and a surface plasmon resonance, is presented for a collision-damped two-level atom near or adsorbed on a metal surface. Effects of the laser bandwidth are included by means of a phase-diffusion model for the driving field. In the weak-field or large detuning limit, the population inversion and resonance fluorescence spectrum are analytically obtained. These quantities along with the surface-induced phase-decay constant of the adatom show strong oscillatory behavior as a function of the adatom–surface distance.

I. INTRODUCTION

Recently there has been considerable interest in the interaction of electromagnetic radiation with surfaces. The experiments which have motivated this present paper are those demonstrating the high intensity of light inelastically scattered from molecules adsorbed on metal surfaces[1] and the surface-enhanced luminescence of an excited molecule fluorescing near or on metals and dielectric fibers.[2–4]

To investigate the basic behavior of the surface-enhanced resonance excitation of a laser-driven quantum system near or adsorbed on a surface, as a first step we calculate the resonance fluorescence spectrum of a two-level atom near or adsorbed on a metal surface. In the surface-free case, i.e., in the absence of a solid surface or when the atom is very far from the surface, resonance excitation of a two-level atom by a laser field has been extensively investigated, using the powerful optical Bloch equations.[5] There has also been interest in surface-enhanced spontaneous emission of two-level atoms near a mirror.[6–9] In this paper, we provide a derivation of the surface-dressed optical Bloch equations. The following factors are taken into account:

(i) Radiative spontaneous decay and stimulated emission produced by both the driving laser field and the reflected electromagnetic field.

(ii) Collisional dephasing of the two-level atom produced by foreign atoms in the gas medium, which constitutes the half-region of the interface.

(iii) The oscillatory behavior of the lifetime of the adatom due to interference between the driving field and the reflected field.

(iv) Surface-induced dephasing of the adatomic transition dipole.

(v) The interaction between the adatom and surface plasmons.

(vi) The random fluctuation of the laser field and its influence on the spectrum.

In Sec. II we derive the surface-dressed optical Bloch equations. In Sec. III we solve the equations in the weak field limit to obtain the population inversion and the resonance fluorescence spectrum. In Sec. IV we present results for these quantities and the surface-induced phase-decay constant of the adatom. Section V is the Summary.

II. SURFACE-DRESSED OPTICAL BLOCH EQUATIONS (SBE)

Let us consider a laser-driven two-level atom near or adsorbed on a metal surface. Although the atom has no dipole moment in its ground state, it can have a significant transition dipole connecting the ground and excited states. The reflected field provided by a metallic mirror and surface plasmon resonance can influence the dynamic behavior and scattering spectrum of the adatom.

To treat this problem we utilize a self-consistent approach. This first involves the determination of the induced transition dipole by quantum mechanics, i.e., the optical Bloch equations. The transition dipole is then used in Maxwell's equations to determine the reflected field, and the reflected field in turn is used in the quantum mechanical procedure to find the transition dipole. The resulting form of the reflected field $\hat{E}_R(t)$ is

$$\hat{E}_R(t) = \mu_{12}\hat{\sigma}_{12}(t)f(d) + \mu_{21}\hat{\sigma}_{21}(t)f^*(d)\ , \tag{1}$$

where d is the distance between the adatom and surface, μ_{ij} is the electric-dipole transition matrix element between the states $|i\rangle$ and $|j\rangle$, $\sigma_{ij} \equiv |i\rangle\langle j|$ is the adatomic transition operator, and $f(d)$ is a distance-dependent function which will be discussed in more detail later.

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THEORY OF REACTIONS AT A SOLID SURFACE

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Abstract

Theories and computational procedures are reviewed for processes involving bond breaking and formation at a solid surface. These processes include reactive scattering, recombination, adsorption and desorption. The article ends with a discussion of theoretical techniques for describing how some of the above processes are induced or modified by laser radiation.

CONTENTS

PROGRESS IN SURFACE SCIENCE, in press (1984)

THEORY OF LASER-STIMULATED SURFACE PROCESSES

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Abstract

Theoretical techniques for describing laser-stimulated surface processes in a vacuum and at a gas-surface interface are presented. For adspecies-surface systems, the laser excitation of vibrational degrees of freedom is considered, and quantum-mechanical and classical models and also an "almost first-principles" treatment of the competition between multiphoton absorption and multiphonon relaxation are discussed. The laser excitation of electronic degrees of freedom is considered with respect to surface states of semiconductors and metals, for the predissociation of diatomic adspecies on metal substrates, for ionization, and for resonance fluorescence of a gaseous atom near a metal. In connection with gas-surface interactions, the influence of laser radiation on diffraction patterns and energy transfer in atom-surface scattering is explored. Collisional ionization and ion neutralization in the presence of laser radiation are discussed. The roles of partial pressure and surface coverage in laser-stimulated surface processes are analyzed. Finally, some ideas on surface waves and annealing are presented.

Contents

Abbreviations

AS	Adspecies-Surface
CCGM	Cabrera-Celli-Goodman-Manson
CW	Continuous Wave
FBZ	First Brillouin Zone
FWHM	Full Width at Half Maximum
GLE	Generalized Langevin Equation
HMP	Heisenberg-Markoff Picture
IR	Infrared
IVR	Intramolecular Vibrational Relaxation
LEPS	London-Eyring-Polanyi-Sato
LSSP	Laser-Stimulated Surface Processes
NFE	Nearly-Free Electron
OBE	Optical Bloch Equations
RLV	Reciprocal Lattice Vector
RWA	Rotating-Wave Approximation
SBE	Surface Bloch Equations
SERS	Surface-Enhanced Raman Scattering
SMF	Surface Magnetic Field
SW	Surface Wave
UV	Ultraviolet
1D	One-Dimensional
2D	Two-Dimensional
3D	Three-Dimensional

1. Introduction

While the field of laser-induced chemical and physical processes in the gas phase can now be regarded as well established,[1-5] the situation with respect to condensed phases, particularly interfaces, is still in its early stages.[1] However, a number of pioneering experiments and theoretical developments have indicated that laser-induced molecular rate processes at a solid surface or at gas-solid or liquid-solid interfaces contain a wealth of new and exciting phenomena. The most visible use of lasers in this regard has come from experiments which suggest new processes in microelectronics.[6] Lasers have been demonstrated to be efficient in the annealing of semiconductors[7] and in stimulating deposition and etching on the dimensions of a micrometer.[8-10] Since the basic mechanisms underlying the observations of the experiments on deposition and etching are associated with molecular dynamics, including energy transfer and reactions, this represents a frontier in

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RESONANCE FLUORESCENCE OF MANY INTERACTING ADATOMS AT A METAL SURFACE

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ABSTRACT

A model of resonance fluorescence of a laser-driven two-level atom near a metal surface is reviewed, and results are shown in the weak-field limit for the population inversion and the power spectrum. Extension of the model to interacting adatoms is discussed in terms of phonon-induced level broadening and adatom migration.

INTRODUCTION

Recently there has been considerable theoretical and experimental interest in the interaction of electromagnetic radiation with surfaces. The perfection of the fatty-acid monolayer assembly technique has led to a series of experiments in which the fluorescence of an excited atom or molecule at a fixed distance from a metal surface (gold, silver and cooper) was measured.[1] Experiments have also demonstrated enhanced luminescence and resonance fluorescence for adspecies on metals (and also on dielectric fibers) as compared to the surface-free molecules.[2,3] In order to understand the excitation-relaxation behavior and resonance fluorescence spectrum of a laser-driven atom near a metal surface, we choose in this paper a simple two-level model for the adatom,

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PRODUCTION OF SHORT-WAVELENGTH (XUV) PHOTONS FROM ION-LASER-EXCITED-SURFACE CHARGE EXCHANGE: Li^{3+},He^{+} + Si(111) SYSTEMS

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ABSTRACT

Semiclassical calculations are carried out for the probabilities of electron transfer for Li^{3+} and He^{+} ions colliding with a Si(111) surface, where a laser is used to excite electrons in silicon from the valence band to surface states. It is shown that with a moderate-power laser, high inversion densities of Li^{2+} and He can be obtained, as necessary for high gain.

INTRODUCTION

It has been proposed[1,2] that some selected charge-exchange processes may serve as a means of achieving population inversion for short-wavelength (VUV and soft X-ray) lasers. In a recent study,[2,3] we have analyzed the possibility of obtaining coherent short-wavelength radiation based on neutralization of positive ions A^{m+} at a semiconductor surface S,

$$A^{m+} + S \rightarrow A^{(m-1)} + S^{+}. \qquad (1)$$

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LASER-INDUCED BOUND STATES AT SURFACES: ION NEUTRALIZATION AND ADSORPTION

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Abstract A laser can be used to generate bound states, both electronic and vibrational, of a foreign atom on a solid surface, and is capable of enhancing processes like ion neutralization and adsorption.

INTRODUCTION

Two mechanisms for laser-generated bound states of a foreign species on a solid surface are discussed. The first, ion neutralization, leads to a bound electronic valence state of a projectile ion that is not degenerate with any electronic band states of the surface, while the second, radiative adsorption, gives a stable vibrational state of an adsorbed atom. The laser intensity plays the dominant role in the first process, whereas in the second a resonantly-tuned frequency is of greater importance.

ION NEUTRALIZATION

In many theories treating neutralization of ions scattered from solid surfaces,[1,2] resonance processes play a dominant role. This kind of resonance is between a discrete state and a continuum level. Thus a valence level of the

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Localized Magnetization Arising from Spin-Dependent Impurity Potentials in the Wolff Model

By THOMAS

K. C. Liu, Kai-Shue Lam, and T. F. George

The Wolff model for localized magnetic moments in dilute alloys is extended to include spin-dependent impurity potentials. Two virtual levels emerge, corresponding to different spin states of the conduction electrons. As a result of this removal of degeneracy, there always exists a more favorable spin polarization for the spin state with the more attractive impurity potential, even in certain circumstances where the original Wolff model yields no magnetization. The results are obtained graphically for various situations. The physical pictures entailed can also be interpreted in terms of the Anderson model.

Das Modell von Wolff für lokalisierte magnetische Momente in verdünnten Legierungen wird erweitert und schließt nun spinabhängige Störstellenpotentiale ein. Zwei virtuelle Zustände, entsprechend den unterschiedlichen Spinzuständen der Leitungselektronen mischen sich. Als Ergebnis dieser Entartungsaufhebung, existiert immer eine bevorzugte Spinpolarisation für den Spinzustand mit dem anziehenderen Störstellenpotential, sogar bei gewissen Umständen, wo das originale Wolffsche Modell keine Magnetisierung ergibt. Für eine Reihe von Fällen werden die Ergebnisse graphisch erhalten. Die anfallenden physikalischen Bilder lassen sich auch mit dem Andersonmodell interpretieren.

1. Introduction

In order to explain the occurrence of localized magnetic moments on dilute iron-group ions dissolved in various 4d transition metals and alloys [1, 2], Anderson [3] in his classic model, introduced a Coulomb correlation energy U for the electrons of opposite spins at the impurity site. He predicted that under certain conditions the correlation interaction splits degenerate electronic levels and thus leads to polarization. Subsequently, this model of Anderson also found wide application in other problems of condensed-matter physics, such as chemisorption [4] and charge exchange scattering from surfaces [5, 6]. As far as the problem of localized magnetic moments is concerned, a distinctly different but complementary point of view was proposed by Wolff [7], who considered the same phenomenon within the context of a scattering problem. In Wolff's theory, the conduction electrons of the 4d elements scatter from the potential due to a single impurity atom. For a virtual state thus created which is sufficiently sharp and colse enough to the Fermi level, the impurity atom then developes an exchange potential, similar to Anderson's correlation energy U, that serves to polarize the electrons in its vincinity.

An important feature in the original Wolff model is that the impurity potential is spin independent. The localized magnetization owes its origin entirely to the exchange interaction between electrons. It is thus worthwhile to inquire into possible additional effects due to the introduction of a spin sensitive impurity potential. Such a potential, for example, would result from the situation where the magnetic ion is already polarized to some extent.

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THEORETICAL ASPECTS OF LASER-INDUCED PERIODIC SURFACE STRUCTURE FORMATION

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ABSTRACT

Laser-induced periodic pattern formation has been observed on a variety of substances. In particular, low-power lasers have been used to deposit a pattern on a metal surface. For a relatively smooth surface grating, this pattern can be explained in terms of a perturbative solution of Maxwell's equations. However, as the surface grating is enhanced by this initial deposition, the perturbation solution breaks down. An alternate non-perturbative solution of Maxwell's equations for such rough surfaces is considered here. Moreover, other possible mechanisms that may assist pattern formation are discussed, such as field-enhanced evaporation and surface migration.

After reduction to 75% this rectangle will measure
size of 4 3/4 x 7 5/8 inches (12.1 x 19.2 cm).

INTRODUCTION

Over the past several years, a number of researchers [1-17] have observed periodic patterns developing on the surfaces of solids that were exposed to laser radiation. These patterns have been seen on various metals, insulators, and both doped and pure semiconductors. Most of these experiments were carried out with Nd:YAG or ND:glass lasers tuned to wavelengths between 1.0 μm and 10.0 μm. To obtain these patterns, laser power densities of between 10 MW/cm^2 and 1 GW/cm^2 were employed. Above this range, surface melting would occur, while below this level, no discernible surface pattern was observed.

This laser-induced periodic surface structure has several characteristics. First, the surface pattern consists of a number of parallel grooves running perpendicular to the $\vec{E}$ field of the incident laser. Second, Oron and Sorensen [8] demonstrated that the underlying surface lattice has no effect on the shape of the laser-induced surface structure. On the other hand, Isenor [6] has shown that the existence of scratches on the surface can have a significant effect on the final surface structure. In fact, if the surface is randomly scratched, no periodic surface structure will form. Both Brueck and Ehrlich [12] and van Driel and his colleagues [13] have also observed the development of a weaker secondary pattern parallel to the incident $\vec{E}$ field. With this secondary structure, the surface takes on a scalloped appearance. Finally, these surface patterns produce large drops in the reflectivity of several metals [3-4].

Most of the work so far has considered laser-induced periodic structures on surfaces that already had a certain composition. Needless to say, this necessitates large laser power densities (greater than 10 MW/cm^2) in order to provide sufficient energy for the surface atoms to rearrange. However, Brueck and Ehrlich [12] showed that only a modest amount of laser power (less than 10 W/cm^2) is needed to establish the periodic surface structure when the constituent atoms are deposited from the gas phase. In particular, they showed that Cd, Zn and Al in organometallic compounds could be photochemically deposited on Si or SiO_2 substrates in ordered arrays.

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RESONANCE FLUORESCENCE AND PHOTON TRAPPING OF TWO ATOMS ON A METALLIC SURFACE

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ABSTRACT

Surface-dressed optical Bloch equations are derived for the purpose of evaluating the resonance fluorescence spectrum of two interacting identical atoms near or adsorbed on a metal surface. The derivation takes into account the influence of reflected photons, dephasing due to atomic collisions, the linewidth of the driving laser field and the resonance excitation of surface plasmons. A unique behavior of the surface-modified fluorescence, not seen in analogous gas cell experiments, is predicted. Under the appropriate circumstance, a photon emitted from one of the two atoms can be trapped by the two-adatom-surface system, and this is studied by means of a theory which treats the atoms and their surface images on the same footing.

INTRODUCTION

There has been interest during the past several years in the following radiation effects at surfaces: (i) the anomalously high intensity of light inelastically scattered from adsorbed molecules [1] and (ii) the oscillatory variation of the lifetime of an excited molecule fluorescing near an interface due to interference effects between photon reflection and absorption at a surface [2]. These phenomena have motivated us to examine the fundamental processes involved in surface-modified excitation of a laser-driven quantum system, and for this purpose we have derived a set of surface-dressed optical Bloch equations to evaluate the resonance fluorescence spectrum of a two-level atom near or adsorbed on a metallic surface. In this paper, we shall first review our work on resonance fluorescence of a single adatom [3-5] and then make an extension to the case of two interacting identical atoms.

The second general topic in this paper is photon trapping. It is well known that the radiation behavior of an atom in the presence of other identical atoms is significantly different from that of the independent atom when the interatomic distance is smaller than the wavelength of the radiation [6,7]. In this case the atoms are correlated via their interaction with the common radiation field and should be treated as a single quantum-mechanical system with internal degrees of freedom [8]. It is equally probable for a photon to be emitted or trapped. The emission process is known as superradiance, where the intensity is proportional to the square of the number of atoms [8]. When the atoms are close to a metallic surface, the photon emitted from one of them can reach another one either by direct transmission or through reflection from the surface, as illustrated by FIG. 1. This situation requires that the atoms and their surface images be considered on the same footing [9,10]. Using this procedure, we shall consider the spontaneous emission from two adatoms on a metallic surface, where it will be shown that a photon can be trapped within the two-adatom-surface system under the appropriate circumstance.

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LASER-INDUCED SURFACE MIGRATION VIA SURFACE PLASMONS

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A classical model coupling a charged adspecies to a laser-induced surface plasmon is presented. Such coupling can enhance the rate and specify the direction of surface migration. For the particular case of an atomic oxygen ion of charge -1 adsorbed on aluminum which is exposed to CO_2 laser radiation of intensity 1 W/cm^2, the velocity of migration (61.3 μm/sec) is five orders of magnitude greater than the usual thermal velocities observed at room temperature.

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Journal of Chemical Physics, submitted

LASER-INDUCED ELECTRON-PHONON PROCESSES ON METAL SURFACES

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Electronic charge transfer from bulk to surface states in metals induced by laser radiation is examined. Due to the position of the Fermi energy, it is necessary to also include phonon excitations. Cross sections for this second-order process are presented. Comparison with the surface excitation in semiconductors is made. It is seen that for metals the required laser frequencies are larger and the cross sections substantially less than for semiconductors.

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RESONANCE FLUORESCENCE OF A TWO-LEVEL ATOM NEAR A METAL SURFACE. II. CASE OF A STRONG DRIVING FIELD

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ABSTRACT

The surface-dressed optical Bloch equations for a two-level atom near a metal surface are solved for the case of a strong driving field. An analytic form is obtained for the adatomic resonance fluorescence spectrum. Due to the multiphoton effects of the surface-reflected field and the surface plasmon resonance, the three-peak spectrum is strongly influenced by the surface. A unique surface-induced asymmetry in the side peaks is revealed.

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CONDUCTIVITY IN SEMICONDUCTORS INDUCED BY VIBRATIONAL-TO-ELECTRONIC ENERGY TRANSFER

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Vibrational-to-electronic energy transfer at a semiconductor surface due to an impinging vibrationally-excited diatomic molecule is considered. By promoting an electron to the conduction band, the transfer of a vibrational quantum leads to electron-hole pair formation. Probabilities around five percent have been calculated for the HCl + InSb and HCl + PbSe systems for thermal collision energies, which are large enough to be observed through measurements of the electrical conductivity.

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Fifth Rochester Conference on Coherence and Quantum Optics

June 13-15, 1983

Abstracts

Fifth Rochester Conference on
COHERENCE AND QUANTUM OPTICS, June 13-15, 1983

Resonance Fluorescence of a Two-Level Atom near a Metal Surface: Surface-Dressed Optical Bloch Equations

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The excitation-relaxation behavior and the resonance fluorescence spectrum of a laser-driven atom near a metal surface are analyzed. The radiation field emitted by the atomic transition dipole is reflected by the metal, which can substantially alter the decay behavior and scattering spectrum of the atom. The reflected field can be expressed as[1]

$$\hat{E}_R(t) = \mu_{12}\hat{\sigma}_{12}(t)f(d) + \mu_{21}\hat{\sigma}_{21}(t)f^*(d), \tag{1}$$

where μ_{ij} is the transition dipole between atomic states $|i\rangle$ and $|j\rangle$, $\sigma_{ij} \equiv |i\rangle\langle j|$ is the atomic transition operator and $f(d)$ is a frequency-dependent and atom-metal distance-dependent (d) function, which can be calculated by the Hertz vectors method.[2] The derivation of the surface-dressed optical Bloch equations (SBE) then involves a self-consistent treatment of the surface-reflected field.

Based on Drude's metal model, the surface-induced phase-decaying constant γ_s for the atom, which appears in the SBE, can be expressed as (assuming the dielectric constant of the medium containing the atom to be unity and γ_s in the unit of the Einstein A coefficient):

(i) for the induced transition dipole oriented perpendicular to the surface

$$\gamma_s = \frac{3\beta^3/2}{(1-\beta^2)^2+\alpha^2}[(1+\alpha^2-\beta^2)F_1^{\perp}(D) + \alpha\beta^2 F_2^{\perp}(D)], \tag{2}$$

(ii) parallel

$$\gamma_s = \frac{3\beta^3/2}{(1-\beta^2)^2+\alpha^2}[(1+\alpha^2-\beta^2)F_1^{\parallel}(D) + \alpha\beta^2 F_2^{\parallel}(D)], \tag{3}$$

where $\beta \equiv \omega_{21}/\omega_{sp}$ is a frequency-dependent parameter, ω_{21} is the atomic transition frequency, ω_{sp} is the surface-plasmon frequency, $\alpha \equiv \delta/\beta\omega_{sp}$, δ is the inverse relaxation time for the metal, and

$$F_1^{\perp}(D) = \sin D/D^3 - \cos D/D^2 \tag{4}$$

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Emission of Short-Wavelength (XUV) Photons from Electron Capture by Ions at an Electronically-Excited Solid Surface

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It has been proposed[1] that some selected charge-exchange processes may serve as a means of achieving population inversion for short-wavelength (XUV and X-ray) lasers. In this study, we analyze the possibility of obtaining coherent short-wavelength radiation based on ion-surface charge-exchange. Observation of weak radiation following such charge exchange has already been reported.[2] However, under normal conditions the probability for such a process is too small for making a laser. We propose that significant enhancement of the charge-exchange probability and consequently of the laser gain can be achieved by electronically exciting the surface exposed to impinging ions.[3,4] Such excitation of a surface can be induced by infrared or visible radiation which effectively promotes bulk electrons to surface bands. This should work for both semiconductors and metals, although the cross sections for surface state excitation are expected to be much higher for semiconductors.[5]

Let us consider electron capture by a positive ion A^{m+} at a semiconductor or metal surface S,

$$A^{m+} + S \rightarrow A^{(m-1)+} + S^{+}. \qquad (1)$$

For certain systems the reaction product $A^{(m-1)+}$ is produced predominantly in an excited state capable of emitting short-wavelength photons. The novel feature of the process (1) is that the capture probability depends significantly on the population of surface electrons which can be controlled by external means. In particular, a large number of bulk electrons can be excited to surface bands by irradiating a surface with a source of appropriate power and wavelength. This leads to significant enhancement of the capture probability and consequently of the laser gain.

As specific examples, we consider two systems:

$$He^{+} + Si(111) \rightarrow He(2^3S) + Si^{+}, \qquad (2)$$

$$He^{2+} + Si(111) \rightarrow He^{+}(3\ell) + Si^{+}. \qquad (3)$$

The first process may represent an efficient way of producing metastable helium atoms. The second produces He^{+} predominantly in the second excited state (3ℓ). Subsequent Balmer α and Lyman β transitions give radiation at $\lambda = 164$ nm and at $\lambda = 25.6$ nm, respectively. The charge-exchange probability is calculated for the two processes (2) and (3), and a discussion is given on the power requirement on the excitation source in order for the probability to be significantly enhanced. Calculations are also reported for the gain coefficients of the Balmer α and Lyman

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MATERIALS RESEARCH SOCIETY

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FINAL PROGRAM
AND
ABSTRACTS

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Paper No. I10.1, Page No. 409

MICROSCOPIC THEORY OF LASER-INDUCED PERIODIC SURFACE STRUCTURE FORMATION.

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Metallic particles resulting from photodissociation of an organometallic gas by a laser can condense as periodic structures (ripples) on a solid surface.[1] A macroscopic mechanism for this phenomenon, where the laser field at the surface generates the ripple pattern, has been advanced. We present a fundamental microscopic theory for the laser-induced periodic surface structure (LIPSS), which includes electronic and vibrational degrees of freedom of the metal/substrate system within a linear-chain approximation. A molecular orbital (MO) approach provides us with electronic wave functions and energies, and the vibrational interaction with the phonons of the solid modifies the latter. The periodic electromagnetic field influences these interactions at each point on the surface modeled as a collection of linear chains. Using the metal-substrate interaction potential, we derive an initial metal deposition rate. The dynamics of subsequent multilayer LIPSS formation is treated using a metal-metal interaction potential obtained by combining MO theory and a nearly-free-electron model. Using information about the gas-phase photodissociation rate, we are able to examine the influence of different laser frequencies and intensities, surface roughness profiles, and gas pressure and temperature.

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1. S. R. J. Brueck and D. J. Ehrlich, Phys. Rev. Lett. 48, 1678 (1982).