ELSEVIER

Physica B 219&220 (1996) 425–427

PHYSICA B

Dynamics of random overlayers

C.S. Jayanthi*, S.Y. Wu, J.A. Cocks

Department of Physics, University of Louisville, Louisville, KY 40292, USA

Abstract

In this paper, a method for studying the dynamics of random overlayers based on the real-space Green's function method is presented. The method provides the framework to carry out a real-space analysis of the surface modes associated with the overlayers. As an illustrative example, the method is applied to a surface alloy system of the type $A_xB_{1-x}/B(1\,1\,0)$ where species A or B forms an FCC metal. Detailed formulation for the calculation of the layer DOSs from the surface to the deeper layers is also presented.

Recently, there has been some concerted effort in the study of disordered surfaces [1–7]. In this work, we are mainly concerned with the development of a methodology to study the vibrational dynamics of a overlayer/substrate system where the overlayer is a disordered alloy. This problem requires a reliable and efficient scheme to treat both the disorder on the surface as well as the loss of the long-range order (LRO) along the direction normal to the surface. We have developed a method of real space Green's function (RSGF) which does not depend on the existence of the LRO [8, 9]. The method provides an extremely efficient and reliable scheme to calculate the local density of states (DOS) [10]. We have successfully applied the method of RSGF to study the dynamics of a relaxed and reconstructed Au(5 1 1) surface [11, 12] and the effect of disorder on the frequency spectrum of Si/Ge alloys [13]. The method is therefore ideally suited for the study of phonons of surface alloys.

To illuminate the implementation of RSGF, we consider the dynamics of surface alloy systems of the type $A_xB_{1-x}/B(1\,1\,0)$ where only the surface layer is disordered, and the atomic species A or B forms a FCC metal. For such systems, reliable force constant matrices can be obtained from the embedded atom method (EAM) [14]. Specifically, we have based our approach on the simple analytic nearest-neighbor EAM model of Johnson [15]. In the present study, we chose to ignore the possible relaxation and reconstruction of the disordered surface and its immediate neighboring layers consistent with the total internal energy derived from the EAM model. Instead, we concentrated our attention to the development of the methodology, which, in the case when the relaxation/reconstruction is taken into consideration, will still be applicable. The Green's function corresponding to the vibrational equations of motion of the overlayer/substrate system is given by

$$G = (z - H)^{-1}, \tag{1}$$

where $z = \omega^2 + i\varepsilon$, and H is the system matrix constructed from the force constant matrices between atoms obtained as second partial derivatives of the total internal energy evaluated at the equilibrium positions. In addition, the fact that there are two different atomic masses on the surface layer has also been taken into consideration in the construction of H.

The starting point for RSGF is to express the system matrix in a block-tridiagonal form [8]. This is always

*Corresponding author.

SSDI 0921-4526(95)00766-0

possible as long as the range of interaction between atoms is finite [10]. For surface-related problems, the most logical way to partition the system matrix is to express it in a layer-by-layer manner [16]. In this situation, an atom in a (1 1 0)-oriented bulk layer with nearest-neighbor interactions interacts only with atoms in its four immediate adjacent layers (two above and two below). To maintain a block-tridiagonal form for the system matrix, one may partition the matrix in terms of shells, with the first shell composed entirely of the disordered surface layer and the subsequent shells each containing two successive layers so that only atoms in the neighboring shells will interact with each other. Each layer matrix is constructed in the real space using the real-space periodicity in terms of N_c $[1\bar{1}0]$-oriented chain matrices with each chain containing N_a atoms. The details of the construction of layer and chain matrices will be given elsewhere [17].

A given configuration of the disordered surface layer is generated randomly according to the atomic concentrations in the surface alloy. The matrix describing a particular configuration c of the overlayer/substrate system can then be expressed as

$$H^c = \begin{pmatrix} h^c_{s1} & V^c_{12} & & & & \\ V^c_{21} & h^c_{s2} & V^c_{23} & & & \\ & V^c_{32} & h^c_{s3} & V_{SB} & & \\ & & V^T_{SB} & h_{SB} & V_{SB} & \\ & & & \cdot & \cdot & \cdot \\ & & & & \cdot & \cdot \end{pmatrix}, \tag{2}$$

where h_{si} denotes the matrix for the ith shell (with a dimension $(6N_aN_c)\times(6N_aN_c)$ for $i \geqslant 2$ and a dimension $(3N_aN_c)\times(3N_aN_c)$ for $i = 1$), and V_{ij} the interaction matrix between shells i and j. For the interactions described by the many-body EAM model, the force constant matrices assume the bulk values from the 5th layer on. Hence the shell matrices from the 4th shell on are designated as h_{SB} and V_{SB}, the respective bulk shell matrices.

The Green's function corresponding to H^c given in Eq. (2) has an exact solution [8, 16]. The shell Green's functions are simply the diagonal blocks of the system Green's function [12, 16]. They can be calculated from the following set of equations:

$$G^c_{s1} = \Delta^+_1 = \{z - h^c_{s1} - V^c_{12}\,\Delta^+_2\,V^c_{21}\}^{-1}, \tag{3}$$

$$G^c_{si} = \{z - h^c_{si} - V^c_{i,i+1}\,\Delta^+_{i+1}V^c_{i-1,i} - V^c_{i,i-1}\,\Delta^-_{i-1}\,V^c_{i-1,i}\}^{-1}, \quad i \geqslant 2, \tag{4}$$

$$\Delta^+_i = \begin{cases} \{z - h^c_{si} - V^c_{i,i+1}\,\Delta^+_{i+1}V^c_{i-1,i}\}^{-1}, & i \leqslant 3, \\ \Delta^+_{SB}, & i \geqslant 4, \end{cases} \tag{5}$$

$$\Delta^-_i = \{z - h^c_{si} - V^c_{i,i-1}\,\Delta^-_{i-1}V^c_{i-1,i}\}^{-1} \tag{6}$$

with

$$\Delta^-_1 = \{z - h^c_{s1}\}^{-1}. \tag{7}$$

From Eqs. (3) – (7), it can be seen that the key to the calculation of the shell Green's functions is the determination of Δ^+_{SB}, which can be calculated by a convergence procedure given in Ref. [16]. It should be noted that the calculation of $\Delta^\pm_i$ and G^c_{si} involves inverting matrices whose dimension is the same as that of h_{si}, much smaller than that of the system matrix. This is the key to the efficiency of our procedure.

The layer DOS of the surface alloy can be obtained as the average surface layer DOS of an ensemble of randomly generated surface configurations. After taking the ensemble average, the layer DOS for the surface and subsequent layers can be determined from the average shell Green's functions using

$$\rho_{l(1)} = -\frac{1}{3\pi}\mathrm{Im}\sum_{j=1}^{3}(\overline{G_{s1}})_{jj}, \tag{8}$$

$$\rho_{l(2i-2)} = -\frac{1}{3\pi}\mathrm{Im}\sum_{j=1}^{3}(\overline{G_{si}})_{jj}, \quad i \geqslant 2, \tag{9}$$

$$\rho_{l(2i-1)} = -\frac{1}{3\pi}\mathrm{Im}\sum_{j=3N_aN_c+1}^{3N_aN_c+3}(\overline{G_{si}})_{jj}, \quad i \geqslant 2, \tag{10}$$

where $\overline{G_{si}}$ is the average ith shell Green's function, $j = 1$, 2, and 3 denote the x ($[1\bar{1}0]$), y ($[0\,0\,1]$), and z ($[1\,1\,0]$) directions respectively, and $\rho_{l(k)}$ is the average layer DOS of the kth layer.

The ensemble average can be carried out straightforwardly by averaging over surface configurations obtained by assigning the atomic species at all the sites on the surface layer according to their concentrations. This process usually requires averaging over a large number of configurations. A much more efficient approach is to set up a random configuration by first concentrating on some arbitrarily chosen site and letting it be occupied by either species A or B with appropriate probability, and then allowing the atomic species at the remaining sites on the surface generated randomly. In this way

$$G^c_{si} = x_A\,G^{cA}_{si} + x_B\,G^{cB}_{si}, \tag{11}$$

where $x_{A(B)}$ denotes the concentration of the atomic species A(B) and $G^{cA(B)}_{si}$ is the ith shell Green's function corresponding to a configuration with the atomic species A(B) on the chosen site and the atomic species on the remaining sites on the surface generated randomly. The average shell Green's function is then given by

$$\overline{G_{si}} = \frac{1}{m_c}\sum_c G^c_{si} \tag{12}$$

with m_c being the number of configurations in the ensemble. Using the recipe given by Eqs. (11) and (12), a reliable average shell Green's function can be obtained by averaging over only a few configurations [13].

An examination of Eqs. (8)–(10) reveals that the average layer DOS gives the average chain (along the x-direction) DOS and also the local site DOS of a typical atom on that layer. Furthermore, $(\rho_{l(k)})_j$ with $j = 1, 2$, or 3 gives the local site DOS along x-, y-, or z-direction. Thus we have developed a reliable and efficient method which provides the mechanism to carry out a detailed analysis of surface phonons for a disordered surface on a substrate, their vibrational characteristics, and their behavior as they go into the bulk. For example, one may first compute the surface layer DOS as a function of the 'impurity' concentration, x_{imp}, identify key vibrational modes, and observe how those modes evolve as x_{imp} varies. Furthermore, one can follow the behavior of those modes on the layer DOS's corresponding to the deeper layers, trace how the bulk behavior sets in, thus obtain an understanding of the interplay between surface and bulk properties. The method is currently being applied to study the surface dynamics of two very different overlayer/substrate systems, namely $Au_xAg_{1-x}/Ag(1\,1\,0)$ [7] and $Au_xNi_{1-x}/Ni(1\,1\,0)$ [18], and the result will be published in a forthcoming paper.

This work is partially supported by the National Science Foundation through Grant No. EHR-9108764 and Grant No. OSR-9452895.

References

[1] A.A. Maradudin and A.R. McGurn, Phys. Rev. B 39 (1989) 8732.
[2] A. Khater, N. Auby and R.F. Wallis, Surf. Sci. 217 (1989) 563.
[3] F. Fabre, G. Armand, J.R. Manson and J Lapujoulade, Vacuum 41 (1990) 427.
[4] D. Kechrakos, J. Phys.: Condens. Matter. 2 (1990) 2937.
[5] A. Khater, H. Grimech, J. Lapujoulade and F. Fabre, Surf. Sci. 251 (1991) 381.
[6] P. Knipp, Phys. Rev. B 43 (1991) 6908.
[7] S. Rousset, S. Chiang, D.E. Fowler and D.D. Chambliss, Phys. Rev. Lett. 69 (1992) 3200.
[8] K.S. Dy, S.Y. Wu and T. Spratlin, Phys. Rev. B 20 (1979) 4237.
[9] S.Y. Wu, J.A. Cocks and C.S. Jayanthi, Comput. Phys. Commun. 71 (1992) 125.
[10] S.Y. Wu, J.A. Cocks and C.S. Jayanthi, Phys. Rev. B 49 (1994) 7957.
[11] A. Kara, C.S. Jayanthi, S.Y. Wu and F. Ercolessi, Phys. Rev. Lett. 72 (1994) 2223.
[12] A. Kara, C.S. Jayanthi, S.Y. Wu and F. Ercolessi, Phys. Rev. B 51 (1995) 17046.
[13] C. S. Jayanthi, S.Y. Wu and J.A. Cocks, Phys. Rev. B 50 (1994) 7992.
[14] S.M. Foiles, M.I. Baskes and M.S. Daw, Phys. Rev. B 33 (1986) 7983.
[15] R.A. Johnson, Phys. Rev. B 39 (1989) 12554.
[16] S.Y. Wu, Zhongliang Xie and N. Potoczak, Phys. Rev. B 48 (1983) 14826.
[17] C.S. Jayanthi and S.Y. Wu, to be published.
[18] L.P. Nielsen, F. Besenbacher, I. Stensgaard, E. Laegsgaard, C. Engdahl, P. Stoltze, K.W. Jacobsen and J.K. Nørskof, Phys. Rev. Lett. 71 (1993) 754.