

Effect of strain on the chemisorption of CO on ultrathin Ni films on Cu(001)

E.-K. Whang and J. Oh

Department of Chemistry, Sook-Myung Women's University, Seoul 140-742, Republic of Korea

S.-K. Kim and J.-S. Kim*

Department of Physics, Sook-Myung Women's University, Seoul 140-742, Republic of Korea

Geunseop. Lee

Korea Research Institute of Standards and Science, Taejon 305-600, Republic of Korea

(Received 12 July 2000; published 22 January 2001)

The chemisorption of CO on ultrathin epitaxial Ni films on a Cu(001) surface was investigated by high resolution electron energy loss spectroscopy (HREELS). CO molecules adsorb on both on-top and bridge sites of the Ni film at room temperature (RT) as is the case on a bulk terminated Ni(001). The vibration energies of CO stretching modes on both sites monotonically increased and grew beyond those on a Ni(001) surface with increasing Ni thickness. The relative population of the two bonding sites gradually changed; the on-top site is preferred by CO for submonolayer Ni coverages while the bridge site is slightly favored for the Ni films thicker than 3 monolayers (ML). We found an existing model, the ‘‘pillow model,’’ for the strain effect on the vibrational energy incompatible with our spectroscopic results.

DOI: 10.1103/PhysRevB.63.075401

PACS number(s): 68.43.-h, 82.20.Pm

I. INTRODUCTION

Heteroepitaxial thin films usually have different atomic structures from their bulk states. As a result, their electronic, magnetic, elastic, and chemical properties are quite different from those of their bulk states.¹ Especially, the strain in the films on the lattice-mismatched substrates affects the chemisorption properties of the films considerably.²⁻⁴ Recently, Gsell *et al.*⁵ studied the adsorption of oxygen atoms on a Ru(0001) surface under inhomogeneous local strain by scanning tunneling microscopy (STM). The oxygen atoms adsorbed preferentially on top of the nanometer-size protrusions above the subsurface argon bubbles, where tensile strain prevails, while they are depleted around the rim of the bubbles, i.e., the region under compressive strain. Hence, it shows a possibility to tailor the chemical properties of surfaces through the adjustment of the surface strain by epitaxially growing metal films on proper, lattice mismatched substrates. It has already been proven important for bimetallic catalysts, where different films upon a substrate may either promote or hinder a surface chemical reaction.⁶

The generality of the effect of strain on surface reactivity and its microscopic origin has been investigated by a series of electronic structure calculations.⁷ The chemisorption energies and the dissociation barriers of CO increased linearly as the tensile strain increases, on several different transition metal surfaces and overlayers. Such results were attributed to the systematic shifts in the *d* bands of the metals induced by the strain. The *d* band shift was also found to correlate with the surface core level shift, which was proportional to the bonding energy of CO.³

Nickel and copper differ in their lattice parameters by 2.5%. The nickel film grows pseudomorphically on Cu(001) in a layer-by-layer fashion, below 6 monolayers (ML).⁸ Thus, the difference in the lattice parameters of the two metals induce tensile strain in the Ni films on Cu(001). Then, we

expect the behavior of the Ni film should be modified from that of the bulk terminated Ni surface due to the tensile stress in the Ni film. For example, the tensile strain strongly influenced the surface phonon dispersion of the pseudomorphic Ni films on a Cu(001) surface. Moreover, a dramatic reduction of the interlayer force constant by 20% and the intralayer force constant by 50% from their bulk values was observed.⁹

The vibrational modes of a chemisorbed species are sensitive to its local bonding environment. This makes vibrational spectroscopy one of the most powerful techniques to investigate the chemical properties of surfaces, encompassing the strained films. Kampshoff *et al.*¹⁰ found a correlation between the surface strain and the shift of the stretching vibration of CO chemisorbed on Cu thin films on various substrates. For Cu films under tensile strain, the energy of the CO stretch mode increases with respect to that on the bulk terminated Cu(001) surface, while it decreases for Cu films under compressive strain. The shift of the CO vibration energy was found to scale linearly with strain in the Cu film.

In this work, we studied the correlation between the surface strain in the Ni films and the vibrational energy and the relative site population of chemisorbed CO molecules on the films by employing high resolution electron energy loss spectroscopy. This work is comprised of four sections. In the next section, experimental procedures are described. We describe the internal vibration energy of CO and the population of each bonding site for different Ni thicknesses at low CO coverage, and then compare the ‘‘pillow model’’ against our spectroscopic results in Sec. III. Then, a summary and conclusion follow.

II. EXPERIMENT

All the experiments were performed in an ultrahigh vacuum chamber with base pressure $\sim 7.0 \times 10^{-11}$ Torr. A

Cu(001) substrate was cleaned by repeated Ar^+ ion sputtering at 2.0 keV for 20 min followed by annealing at 400 °C for 15 min. The clean surface displayed a sharp $p(1 \times 1)$ low energy electron diffraction (LEED) pattern, and no vibration peaks associated with likely contaminants such as sulfur or carbon were detected. The vibration spectra were obtained by a commercial electron energy loss spectrometer (LK2000).

The thin Ni films were deposited on a Cu(001) substrate at room temperature by thermal evaporation of Ni from a Ni block (purity 99.999%) wound around a tungsten filament (purity 99.99%). The pressure during the evaporation was kept below 2.0×10^{-10} Torr. The thickness of the thin film was estimated by a quartz microbalance located in a position equivalent to that of the sample surface. The deposition rate of Ni was typically around 1 ML per 4 min. We find very minor degradation of the $p(1 \times 1)$ LEED pattern for the Ni films up to 6 ML in regards to the low background intensity and the sharpness of the LEED spots. The cleanliness of the Ni film was also checked by HREELS.

CO molecules were dosed onto the Ni films at room temperature through a conventional leak valve. During the CO dosage, pressure was maintained at 1×10^{-8} Torr. The formation of a $c(2 \times 2)$ adlayer required 2 to 4 Langmuirs (1 Langmuir = 1 L = 10^{-6} Torr sec) of CO dosage depending on the thickness of the Ni film.

The vibration spectra were measured at room temperature in a specular geometry with its angle of incidence 60° from the surface normal. The resolution of the spectrometer was 4–5 meV, estimated from the full width at half maximum (FWHM) of the elastic peak in the specular geometry. All the data reported here were measured with primary electron energies (E_0) less than 10 eV to minimize possible electron stimulated disruption of the adsorbed CO molecules.

III. RESULTS AND DISCUSSION

Figure 1 shows the vibration spectra of the CO stretching mode for various thicknesses of the Ni films. All the spectra were taken with 1 L of CO dosage, which corresponds to the CO coverage below 0.5 ML, because the $c(2 \times 2)$ superstructure is observed with more than 2 L of CO dosage. Such a low coverage limit of CO was intended to focus on the local bonding property of CO with nearby Ni atoms by minimizing the dipole-dipole interaction between CO molecules. The two loss peaks observed in the range of 1800–2100 cm^{-1} are the C-O stretching modes, the lower energy one from CO at the bridge (b) site, $\nu(\text{C-O})(\text{b})$, and the other at the on-top (t) site, $\nu(\text{C-O})(\text{t})$. The adsorption sites of the CO molecule were assigned by comparing their energies with those on bulk Ni(001) surface.¹¹

There are two features that show dependence on the thickness of the Ni film. First, $\nu(\text{C-O})$ increases from 2020 cm^{-1} to 2058 cm^{-1} for the CO(t), and from 1912 cm^{-1} to 1940 cm^{-1} for the CO(b) as the thickness of the Ni film increases as summarized in Fig. 2. The energy of each loss peak was obtained by a curve fitting procedure employing a Gaussian peak for each peak. For the 6 ML film, the vibration energies of CO at both sites are larger than those at the Ni(001) sur-

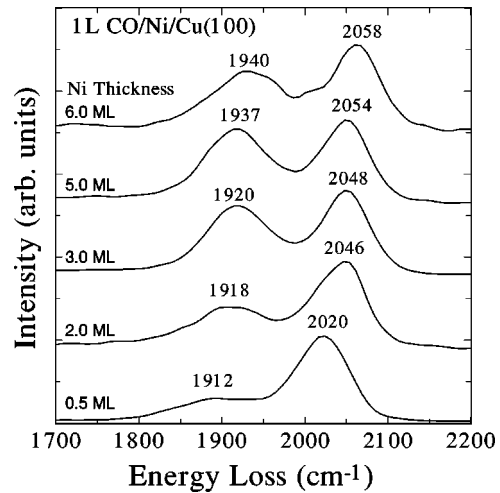


FIG. 1. The stretching spectra of the CO molecules at both the bridge and the on-top sites of the Ni films on Cu(001). The primary electron energy for the HREELS measurement is 3.0 eV. The angle of incidence is 60° from the surface normal direction.

face. Second, the loss intensity at the bridge site increases with increasing Ni film thickness, and becomes comparable with that at the on-top site for $\Theta_{\text{Ni}} \geq 3$ ML (Fig. 3). That is in sharp contrast to the behavior on the bulk terminated Ni(001) surface, where CO adsorbs predominantly on the on-top site at RT.¹²

We can think of two physical origins that would determine the behavior of the CO molecule on Ni films. First, the electronic structure of the Ni film is influenced by the hybridization with the electronic states of the Cu substrate.^{13–17} Aside from the hybridization effect, the electronic structure of the Ni film is also affected by the tensile strain in the Ni film. For thin films in the monolayer regime, these two ef-

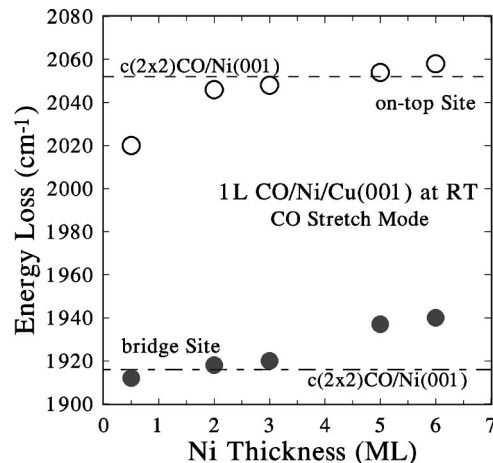


FIG. 2. The vibration energies of the CO stretching mode as a function of Ni thickness for both (a) the bridge and (b) the on-top site. The error limit in the curve fitting procedure is ± 2 cm^{-1} . No statistical error limit was attempted due to the small number of data. Dashed horizontal lines signify the $\nu(\text{C-O})(\text{t})$ and (b) on a bulk terminated Ni(001). The primary electron energy for HREELS measurement is 3.0 eV. The angle of incidence is 60° from the surface normal direction.

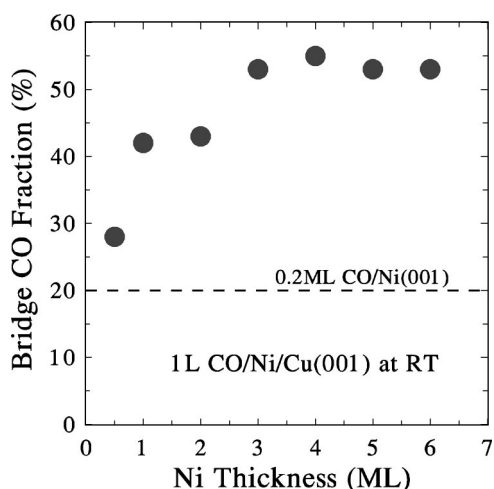


FIG. 3. The fraction of CO molecules adsorbed at the bridge site of the Ni films on Cu(001) as a function of the Ni thickness. No statistical error limit was attempted due to the small number of data for the statistical analysis. The error limit in the curve fitting procedure is less than $\pm 5\%$. The dashed horizontal line is the bridge fraction of CO on bulk terminated Ni(001). The primary electron energy for HREELS measurement is 3.0 eV. The angle of incidence is 60° from the surface normal direction.

fects are intermingled and make the microscopic picture hard to attain. As the film gets thicker, however, the interface effect or the hybridization effect gets weaker, and the strain effects would single out and determine the chemisorption property of the Ni film. Hence, we would concentrate on the adsorption of CO mainly on the thick Ni films such as the 6 ML film, where the strain effect should dominate. $\nu(\text{C-O})$ is still increasing, even going from 5 to 6 ML films (Fig. 2), which implies that the interface effect still remains.¹⁸ To find solely the strain effect, we should take the thicker sample, which would give the higher vibration energy as expected from the uptake trend. From 6 ML, however, the Ni film starts to get rough,⁸ and the roughness of the film was reported to change the vibration energy in such a way that the smoother the surface, the higher the vibration energy of CO.¹⁰ The CO stretching energy on Cu clusters differs from that on the flat surfaces of Cu films by 10 to 15 cm^{-1} . Such a roughness effect would be more severe for the more reactive Ni film. Hence, we limited our Ni film below 6 ML.

For the 6 ML thick Ni film, $\nu(\text{C-O})(b)$ is 1940 cm^{-1} and $\nu(\text{C-O})(t)$ is 2058 cm^{-1} . For CO coverage below 0.5 ML, there are several reports on the stretch modes of CO on the bulk Ni(001) surface.^{11,19-21} For CO(t), the reported vibration energies range from 2000 to 2048 cm^{-1} , while that at the bridge site is from 1876 to 1916 cm^{-1} . We do not know, however, the coverage of CO for each reported system. Since the vibration energy increases with CO coverage,²² we cannot directly compare the reported values with ours. Instead, we took the vibration energies from the well-defined $c(2 \times 2)$ adlayer on bulk Ni(001) by Andersson,¹¹ i.e., 1916 cm^{-1} (bridge site) and 2052 cm^{-1} (on-top site) as an upper limit, and compared them with those of our 1 L dosage data, for which no $c(2 \times 2)$ superstructure is formed and CO coverage is definitely below 0.5 ML. We still find that for both

adsorption sites, CO vibration energies are larger on the 6 ML Ni film than the corresponding vibration energies on a bulk Ni(001) surface.

The difference of the CO stretch energies between those on the 6 ML Ni film and on bulk Ni(001) is $+6 \text{ cm}^{-1}$ for the on-top site, smaller than the difference at the bridge site, $+24 \text{ cm}^{-1}$. This tells us that the bridge site is a more sensitive position to detect the strain effect. The bridge site is farther from the atomic core than the on-top site. Then, the local density of states and the bonding angle of the CO with the nearby Ni atoms should be more severely modified on the bridge site than on the on-top site by the tensile strain in the Ni film. This argument is supported by the observation of the huge ($\sim 30\%$) reduction of oxygen vibration energy on Ni films on a Cu(001) surface compared to that on a Ni(001), where the oxygen sits on the fourfold hollow site, farthest from the atomic core.²³ In that bonding site, an oxygen atom most seriously suffers from the modification of the local electronic structure and the bonding angle with the nearest Ni atoms by the tensile strain.

Kampshoff *et al.*¹⁰ found a linear relationship between the strain and $\nu(\text{C-O})(t)$ on various Cu films. The vibration energy increases under tensile strain and vice versa. A microscopic picture of the observation, the so-called, ‘‘pillow model,’’ was given, which purports that the bonding of CO to Cu surface is governed by the σ bonding between Cu $4sp\sigma$ and CO 5σ orbitals and by the π bonding between Cu d_{xz}, d_{yz} and CO $2\pi^*$ states. Tensile strain expands the lattice and decreases the electronic density in the Cu film, which results in the reduced backdonation to the antibonding $2\pi^*$ orbital. Then, the C-O bond stiffens on the tensile strained film, and $\nu(\text{C-O})$ on the film is higher than that on the unstrained surface.

For the Ni film, π bonding also occurs between the d_π orbitals of Ni and the CO $2\pi^*$ orbital exactly as for the case of Cu-CO bonding.²⁴ Hence, the pillow model predicts that $\nu(\text{C-O})$ on the thick Ni films on Cu(001) should be larger than that on bulk Ni(001) surface, which is what we observed in the current experiment.

Even though the intuitive pillow model explained the dependence of the CO stretching energy on the lattice strain quite consistently, it is not compatible with recent theoretical and experimental works on the dependence of chemisorption energies on the lattice strain.^{3,5,7} The pillow model predicts the reduction (increase) of the bonding energy of CO where there is tensile (compressive) strain, because the tensile (compressive) stress expands (reduces) the lattice, which results in the reduction (increase) of the bonding charge density. In contrast, recent *ab initio* total energy calculation predicted the strengthening of CO and O bonding on some transition metal surfaces under tensile stress, because the centroid of the d band shifts toward Fermi energy, compensating the narrowed d band width due to the expansion of the lattice.⁷ Such a prediction is consistent with the observation that on the films under tensile strain, the surface core level associated with the d band shifts toward the lower binding energy side and the thermal desorption temperatures of CO on those films increase accordingly.³ Gsell *et al.* also reported a preferential bonding of oxygen atoms on the area

under tensile stress.⁵ Thus, it is desirable to study how the bonding energy of CO depends on the lattice strain together with the dependence of $\nu(\text{C-O})$ on the strain to test the validity of the pillow model.

CO molecules adsorb at both the on-top and the bridge sites on Ni(001) surface. Hence, it offers a unique opportunity to study the strain effect on both the vibration energy and the *relative* bonding energies of CO simultaneously. The $\nu(\text{C-O})$ shifts upward more for CO(b) than for CO(t) on the 6 ML Ni film as described before. According to the pillow model, this implies that the C-O bond is strengthened more and, in turn, the backdonation from the Ni film to the antibonding CO $2\pi^*$ orbital decreases more, or π bonding between Ni and CO weakens more for CO(b) than for CO(t). Since the bonding energy of CO is dominated by π bonding,⁷ we expect a larger reduction of the bonding energy between Ni and CO at the bridge site than at the on-top site of the Ni film. It means that *the relative population of CO at the bridge site on the Ni film should be smaller than that on the bulk terminated Ni(001)*, if the pillow model is correct.

We examined the above prediction of the pillow model on the site population. The relative population of the two bonding sites of CO, on-top and bridge sites, is also dependent on the thickness of the Ni film as seen in Fig. 1. For the 0.5 ML Ni film, CO adsorbs predominantly at the on-top site. As the thickness of the Ni film increases, the bridge site population becomes comparable to that of the on-top site beyond 3 ML. This trend is summarized in Fig. 3. Here, each CO coverage is determined from the integrated area of the respective loss peak, assuming that the dynamic dipole moments of CO on both sites are the same. This assumption has been proven to be the case by infrared reflection absorption spectroscopy (IRAS) studies for CO coverage below 0.5 ML on the bulk Ni(001) surface.^{19,20}

Grossmann *et al.*²² investigated the adsorption of CO on bulk Ni(001) at RT by IRAS, varying CO coverage from 0 to 0.8 ML. They found that the maximum bridge fraction is less than 30%. Lauterbach *et al.*¹⁹ also report a similar maximum value for the bridge fraction. Then, the pillow model predicts that the bridge fraction of the CO population on the Ni film should be lower than 30%, whatever the CO coverages are in our experiment (it is definitely below 0.5 ML for our case). In contrast, the bridge fraction is $\sim 55\%$ for the Ni films (≥ 3 ML), higher than the maximum bridge fraction on a bulk Ni(001), 30%. Thus, we find that the pillow model is not adequate for explaining the strain effect on the adsorption energy.⁷

Before concluding the issue on the site population, we want to mention on the effect of contaminants. Grossmann *et al.*²⁰ observed that contaminants such as sulfur, oxygen, and carbon catalyze the occupation of the bridge site to the on-top site. We cannot preclude the existence of contaminants on the film. Our experiments were, however, performed while maintaining low base pressure and evaporation pressure. Moreover, in HREELS spectra, no peaks associated with contaminants were observed. Sometimes, we can find weak structures near the loss energy 700 cm^{-1} and 1200 cm^{-1} , which is attributed to hydrogen.²⁵ Hydrogen precov-
erage is, however, known not to affect the site population of

CO on the Ni(001) surface.²⁰ In our work, the spectra with and without the hydrogen feature did not make any noticeable change, either. Hence, we can tell that the dramatic increase of the bridge site population is not driven by contaminants, and our conclusion on the invalidity of the pillow model should be reliable.

This work has attempted to test the proposed models on the effect of lattice strain against both the vibrational energy shift and the bonding energy. We found that the pillow model was not a successful model in its pristine form to explain both. Furthermore, it contains inherent weaknesses in some of its assumptions. First, it assumes that the $\nu(\text{C-O})$ scales with the bonding energy of CO. Vibrational energy is, however, dependent not on the strength of the corresponding bond, but on the shape of the bonding potential. Recent *ab initio* calculations of the CO stretching energy on Ru(0001) surface under various lattice strain²⁶ found that (1) there appeared to be no correlation between bonding energy and vibrational energy of CO and (2) there was a nonlinear and unpredictable relation between vibrational frequency and lattice strain. Thus, it would not be correct to assume that a stronger bound CO on a surface will show a vibrational frequency lower than that of a weaker bound CO on the same surface. Second, it assumes that the bond charge and the bonding energy of CO is reduced (increased) under tensile (compressive) strain. This picture does not take into account the relaxation of the strained film, the modification of the bonding position of CO on the strained surface, and the resulting change of electronic structure and bonding charge density, which would affect the bonding energy of CO. In fact, the enhanced bond strength has been reported on the tensile stressed surface.^{3,5}

The pillow model tacitly assumes the validity of the Blyholder model. Thus, we may also suspect that the Blyholder model, rather than the pillow model, does not work and provides inconsistent predictions of the vibration energy and the site population of CO on Ni films. However, we think that the Blyholder model is still valid for CO chemisorption on Ni film on the following grounds; The Blyholder model is known to explain CO chemisorption on bulk terminated Ni(001), reasonably well.²⁴ Besides, for a 1 ML Ni film on Cu(001), the Fermi surface is known to be virtually identical to that of bulk terminated Ni(001).¹⁵ Thus, the bonding mechanism of CO on Ni film should be similar to that on bulk terminated Ni(001), and we expect the Blyholder model also works for CO bonding on the Ni film. Furthermore, the validity of this rather simple model has been corroborated by a recent theoretical study of CO chemisorption on various transition metal substrates.⁷ Therefore, the Blyholder model, despite its simplicity, is expected to be a widely applicable model for CO–transition metal bonding. Hence, it would not be the Blyholder model but the pillow model that should be responsible for the wrong prediction of CO chemisorption on Ni film.

There still remains a question why the empirical, linear relation between the CO stretching energy and lattice strain is so widely observed for Cu films and consistently described by the defunct pillow model.¹⁰ The pillow model emphasizes the overlap of wave functions in the bonding of CO and

substrate, while the d band shift model, based on an *ab initio* result, stresses the role of the denominator in the coupling matrix, which is the energy difference of two bonding orbitals. The above-mentioned two terms combined, however, determine the strength of the bonding. A more refined, comprehensive picture reconciling both factors is still awaited and hoped for to explain the observed effect of strain on CO chemisorption.

IV. SUMMARY AND CONCLUSION

CO vibration spectroscopy on ultrathin Ni films on Cu(001) was carried out by HREELS in the low CO coverage limit at RT. CO molecules adsorbed on both the on-top and the bridge sites at RT as it did on bulk terminated Ni(001). Both the population and the vibration energy of CO on the Ni film showed a notable dependence on the thickness of the Ni film. For 6 ML thick Ni films, the stretching vibration energy of CO was larger at both bonding sites than those on Ni(001). The effect was larger for the bridge site, suggesting that the site is more sensitive for strain. The site preference changed from the on-top site to the bridge site for Ni

films thicker than 3 ML. This is in sharp contrast to the dominant occupation of the on-top site on bulk Ni(001) at RT. The pillow model explained the vibrational energy shift of CO under strain, but failed to explain the relative site population of CO. We still lack a comprehensive understanding of the microscopic mechanism controlling how the strain affects chemisorption of CO. For the thinner films, both the hybridization and strain effect come together to determine the chemisorption properties of Ni film, making a microscopic picture harder to grasp. From the rapid variation of the vibration energy and the site population, we expect a variety of chemical properties for thin Ni films determined by the strain and the hybridization effects.

ACKNOWLEDGMENTS

J.K. acknowledges B. Hammer and J. Lee for careful comments, M. Mavrikakis for releasing unpublished results with detailed comments, and J. Seo for technical support. This work was supported in part by KOSEF through ASSRC and by the Ministry of Science and Technology under Grant No. 99-N6-02-01 (J.K.).

*Electronic address: jskim@sookmyung.ac.kr

¹E. Bauer and J.H. Van der Merwe, Phys. Rev. B **33**, 3657 (1986).

²P. Biberian and G.A. Somorjari, J. Vac. Sci. Technol. **16**, 2073 (1979).

³J.A. Rodriguez and D.W. Goodman, Science **257**, 897 (1992).

⁴J.H. Larsen and I. Chorkendorff, Surf. Sci. **405**, 62 (1998).

⁵M. Gsell, P. Jakob, and D. Menzel, Science **280**, 717 (1998).

⁶John H. Sinfelt, Rev. Mod. Phys. **51**, 569 (1979).

⁷M. Mavrikakis, B. Hammer, and J.K. Nørskov, Phys. Rev. Lett. **81**, 2819 (1998); B. Hammer, Y. Morikawa, and J.K. Nørskov, *ibid.* **76**, 2141 (1996).

⁸J. Shen, J. Giergiel, and J. Kirchner, Phys. Rev. B **52**, 8454 (1995).

⁹Y. Chen, S.Y. Tong, J.-S. Kim, M.H. Mohamed, and L.L. Kesmodel, Phys. Rev. B **43**, R6788 (1991).

¹⁰E. Kampshoff, E. Hahn, and K. Kern, Phys. Rev. Lett. **73**, 704 (1994).

¹¹S. Andersson, Solid State Commun. **21**, 75 (1977).

¹²A. Grossmann, W. Erley, and H. Ibach, Phys. Rev. Lett. **71**, 2078 (1993).

¹³J. Tersoff and L.M. Falikov, Phys. Rev. B **26**, 6186 (1982).

¹⁴D.-S. Wang, A.J. Freeman, and H. Krakauer, Phys. Rev. B **24**, 1126 (1981).

¹⁵G.J. Mankey, K. Subramanian, R.L. Stockbauer, and R.L. Kurtz, Phys. Rev. Lett. **78**, 1146 (1997).

¹⁶M.A. Abu-Johdeh, B.M. Davies, and P.A. Montano, Surf. Sci. **171**, 331 (1986).

¹⁷K. Kishi and T. Fujita, Surf. Sci. **227**, 107 (1990).

¹⁸The surface stress of the Ni film on Cu(001), prepared with similar deposition condition as ours, was reported to be nearly constant up to 12 ML of Ni film [D. Sander, Rep. Prog. Phys. **62**, 809 (1999)]. For the thicker Ni film, the stress becomes smaller with the formation of dislocations. Thus, the dependence of the vibration energy on the thickness of the film does not derive from the varying strain of the Ni film.

¹⁹J. Lauterbach, M. Wittmann, and J. Kupperts, Surf. Sci. **279**, 287 (1992).

²⁰A. Grossmann, W. Erley, and H. Ibach, Appl. Phys. A: Solids Surf. **57**, 499 (1993).

²¹R.G. Tobin, S. Chiang, P.A. Thiel, and P.L. Richards, Surf. Sci. **140**, 393 (1984).

²²A. Grossmann, W. Erley, and H. Ibach, Surf. Sci. Lett. **330**, 646 (1995).

²³J.-S. Kim, M. H. Mohamed, and L.L. Kesmodel, Surf. Sci. **260**, 185 (1992).

²⁴R. Hoffmann, *Solids and Surfaces: A Chemist View of Bonding in Extended Structures* (VCH, New York, 1988), p. 71.

²⁵W. Erley, H. Ibach, S. Lehwald, and H. Wagner, Surf. Sci. **83**, 585 (1979).

²⁶M. Mavrikakis (private communication).