

**HRLEED STUDY OF THE ROUGHENING TRANSITIONS IN
Cu (110), Ni(110) AND Ag (110) SURFACES**

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HRLEED STUDY OF THE ROUGHENING TRANSITIONS IN Cu(110), Ni(110) AND Ag(110) SURFACES.

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ABSTRACT

We present the results of High Resolution Low Energy Electron Diffraction (HRLEED) measurements of the thermal roughening transition on Cu(110), Ag(110) and Ni(110) surfaces. We performed careful spot profile intensity measurements as a function of temperature. We observed a proliferation of steps along the (110) and (001) directions. In addition a strong deviation from a Debye model was observed in the scattered intensity of the Bragg reflections. This deviation from the harmonic approximation occurs well below the roughening transition temperature. The behavior of the three metal surfaces is qualitatively similar except for the transition temperatures. Ni shows the highest transition temperature (1300 K), Cu is intermediate (1000 K) and Ag has the lowest temperature (730 K). Analyzing the behavior of the (00) reflection intensity, and the evolution of the line shape as a function of the temperature, we found clear evidence of a roughening transition at the (110) surface. A lineshape analysis of the (00) reflection shows the transition from a Lorentzian lineshape to a power law. We also proved, based on the experimental data and a recent theoretical model, that there is a tremendous increase in step density and a decrease in the average terrace size as the temperature increases. We used STM to corroborate the HRLEED results at room temperature. We found excellent agreement.

INTRODUCTION

The study of the structure and thermal behavior of a crystal surface is of great importance in many areas of science and technology. The concept of surface roughening transition was first raised many years ago by Burton, Cabrera and Frank[1]. Since then it has played a central role in the theories of crystal growth and equilibrium crystal shapes. A surface roughening transition for a crystal surface occurs at a critical temperature at which the surface evolves from a low temperature smooth phase to a high temperature rough phase. The smoothness and roughness are defined by the height correlation function of the surface, if the asymptotic limit of the correlation function goes to a constant, the surface is smooth; if it diverges, the surface is rough. On the atomic level, this transition results from the proliferation of atomic steps, islands or kinks on the crystalline surfaces. A considerable amount of work has been done to study this phenomenon[2]-[18]. Experimentally, in the last few years, roughening transitions have been observed by He-atom, X-ray and low energy electron scattering experiments on the vicinal and (110) fcc metal surfaces. These studies have shown strong evidence of roughening transition on vicinal (11 n) surfaces far below the bulk melting temperature, and the (110) surfaces have also been observed undergoing roughening transitions below the bulk melting temperatures, but the interpretation of the experimental results for (110) surfaces are often controversial. Some disagreement exists on the nature of the transition and on the transition temperature itself.

We have investigated the roughening transition on the (110) surfaces of the fcc metals copper, nickel and silver. For Cu(110), X-ray diffraction studies have indicated the existence of a surface roughening transition near 870K, however, the He-scattering detected no evidence of roughening transition for Cu(110) surface up to 900K, instead ascribing the observed anomalous thermal behavior to surface anharmonic effects. More recently, a study of Ni(110) was reported, inspired by the roughening transition observed

on the Ni(113) surface[9]. This study indicated that anharmonicity develops above 900K on the Ni(110) surface and that a roughening transition occurs near 1300K. For Ag(110), the observation of roughening transition have been reported by X-ray [12] and He-atom scattering [17] while the interpretation of the transition itself and the transition temperature remain a matter of dispute. However, none of the above studies have connected quantitatively the surface roughening transition with the distribution of the steps on the surfaces which is crucial to explain a surface roughening transition. In our study, we have not only observed the roughening transitions on these surfaces, we also give quantitative results on the step distribution as function of temperature. The techniques involved in our experiments are the surface sensitive High-Resolution Low-Energy Electron Diffraction(HRLEED) and Scanning Tunneling Microscopy(STM).

EXPERIMENT

The experiments were conducted in an ultra-high-vacuum(UHV) system with a base pressure less than 10^{-10} Torr. The system consists of a high precision manipulator which can be moved in translation along three (x,y,z) orthogonal directions and tilted in x-y plane by a rotation rod. The heater embedded in the manipulator, with the options of resistive and direct heating, can heat the sample up to 1300K. The temperature was measured using two Chromel/Alumel thermocouples and an optical pyrometer. An argon ion sputtering gun is attached to the chamber which can be used to clean the sample surface. The system also includes a load lock chamber which is used to introduce samples into the analysis chamber without destroying the vacuum. We have two instruments mounted in the main chamber a High-Resolution Low-Energy Electron Diffraction (HRLEED) system and Scanning Tunneling Microscopy (STM).

Low-Energy Electron Diffraction(LEED) is a widely used technique in the studies of crystal surfaces. It can probe the long-range order of periodic surface structures. For electrons with energy between 50-500eV, the penetration length is a few angstroms which is only a few atomic layers. So the diffracted electrons will carry mainly information from the surface. Qualitative information can be obtained by a visual inspection of the LEED pattern on the screen of a LEED system, so the arrangement of the LEED spots on the screen characterizes the size and shape of the unit mesh for the substrate(normal spots) as well as for the adsorbate layers(extra spots). The integral intensity of LEED spots as a function of the electron energy(I/V curve) provides the quantitative information on the atom arrangement within the unit mesh. These methods have been successfully applied to ideal surfaces. However, most surfaces contain some kind of defects. The information on the defects can be obtained by analyzing the spot profile, i.e., the angular distribution of the intensity of the LEED spot. But conventional LEED system has its limitations in terms of getting accurate spot profile due to its relatively low K resolution. High resolution LEED has to be used. Compared to conventional LEED, HRLEED has a much higher K resolution[19-24].

STM is a complementing technique in this research. We used it to image the surface in real space to corroborate the result from HRLEED experiments.. One of the most notable achievements of STM is the elucidation of the atomic arrangements of various surfaces. Many disputed surface structural models which were studied by various experimental techniques and theoretical calculations have been resolved by the direct imaging capability of the scanning tunneling microscopy.

The copper sample is a single crystal with (110) surface exposed. It is in the form of a disk with a 5mm diameter, 1mm thickness. Before introducing it into the UHV chamber, the surface was mechanically polished, then etched using a 50% phosphoric acid solution. After etching, it was rinsed with a 10% phosphoric acid solution, then with distilled water, finally blow dried with nitrogen. Before each experiment, the in-situ cleaning procedure was performed. The surface was first sputtered by argon ions to strip off a few layers in

order to get rid of the surface contamination, mostly oxygen, carbon and sulfur. Since a sputtering procedure generally created a disorder surface, annealing was performed to recover the ordered surface.

The Ni(110) sample is in the form of a disk with a 10mm diameter, 2-3mm thickness. Before the sample was introduced into the chamber, it was mechanically polished then etched with a 2:1 sulfuric acid solution. After etching, it was rinsed with distilled water and blow dried with nitrogen. Great care was taken in eliminating the sulfur impurities from the nickel surface.

The Ag sample was spark cut from a silver single crystal cylinder with the (110) surface exposed. The Ag(110) sample is a 9mm x 9mm square with 1.5mm thickness. Before introducing the sample into the chamber, it was mechanically polished then etched with 35% nitric acid solution. The clean Ag(110) surface was obtained by sputtering the surface with argon for 10 minutes, followed by annealing.

RESULTS

Cu(110): The temperature dependence of the surface structure has been studied by a variety of experimental techniques. LEED and RHEED experiments[15] found that at temperatures higher than 673K, both bulk and surface Debye temperatures were anomalously reduced, the surface Debye temperature was reduced faster than the bulk. The average Debye temperatures determined by LEED and RHEED experiments are around 350K and 190K for the bulk and the (110) surface, respectively. The abnormal decrease of the Debye temperature is suggestive of some level of surface anharmonicity on Cu(110). But surface anharmonicity alone could not explain all the observed phenomena, a roughening transition has to be considered as a possible explanation.

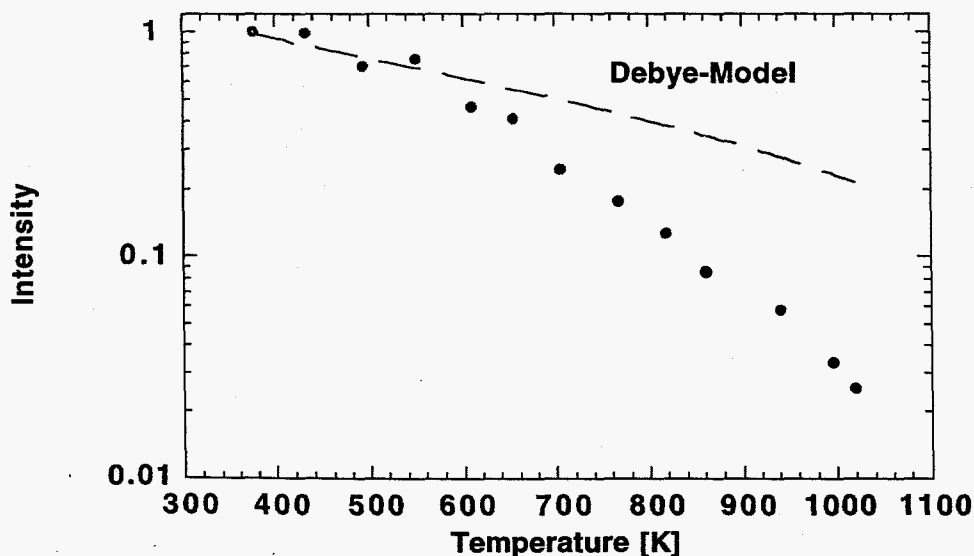


Figure 1. Integrated intensity of the (00) spot vs T (along [001]).

In figure 1 we show the integrated intensity of the (00) spot vs. temperature, the solid line is the Debye theory and the dots are the experimental data. It is noticed that above $T=550\text{K}$, there is an obvious discrepancy between the Debye model and the experiment. We suppose

that the effect of the temperature is not only to make the atoms vibrate around their equilibrium positions but also force some of them out of their equilibrium positions to create defects such as adatoms, vacancies, steps, kinks, etc. These structural disorders will increase as the temperature goes up and will cause a significant decrease of the Bragg peak. But, we can rule out the effect of point defects such as adatoms and vacancies, since these defect structures would give a uniform background instead of the broad diffuse intensity localized in the vicinity of the Bragg diffraction peak. Another possible reason for the abnormal thermal behavior is anharmonic effects. Anharmonicity is a phenomenon which precedes the roughening transition. It could be one of the possible driving mechanisms for the roughening transition. In order to investigate the transition in more detail we performed measurements at out-of-phase conditions.

At out-of-phase condition, the diffraction spot consists of a Bragg central peak and the diffuse tails by the scattering from the surface defects such as terraces and steps. The criteria of a roughening transition are: the integrated intensity of central component drops to zero at the transition temperature and the line shape of the spot profile evolves from Lorentzian to power-law as the temperature approaches the transition temperature. The exponent of the power-law increases as the temperature goes up and equals to 1 at the transition temperature. At an atomic scale, the proliferation of atomic steps is characteristics of a roughening transition. The angular profile of a diffracted beam contains the information on surface defects, so it is important to know how different kind of defects affect the shape of the spot profile. Henzler[20-21] has summarized the general feature of the profile from different kinds of defects. Diffraction from a surface with steps leads to a periodic modulation on the profiles with the changing of the momentum transfer (or incident energy). Lu and Lagally [25], based on the random probability model and boundary-structure-factor analysis, gave a quantitative result on the relationship between the angular profile and the momentum transfer. We use the random probability model to calculate the step density on the surface at different temperatures. The model is based on the assumption that there is no interaction between the steps on the surface, i.e. the event of having a step on one position is independent of the event of having another step on another position. This random occurrence of steps is described by a geometric distribution function. We observed that the step density increases about 200% from 300K to 883K along $[1\bar{1}0]$ direction and the step density increases 100% from 300K to 883K along $[001]$ direction. As a consequence of the increased step density, the average terrace area decreases. The average terrace area decreases by about 84%. We need to point out that the HRLEED result was obtained by assuming monatomic steps on the surface at all temperatures. Actually, the higher the temperature, the more probability we have for multilevel steps on the surface. Considering this factor, the calculated increases on the step density should be even higher. Based on the above results, we are of the opinion that indeed a surface roughening transition occurs on Cu(110) around $T=1000\text{K}$.

Ni(110) and Ag(110): We also studied the thermal behavior of the surfaces of Ni(110) and Ag(110) by analyzing the HRLEED (00) spot integrated intensity as a function of temperature (Figures 2 and 3). We found a deviation from the Debye model for Ni(110) at high temperatures. This abnormal thermal behavior was ascribed to the step proliferation combined with surface anharmonicity. The line shape of the (00) spot profiles were analyzed as a function of temperature and the evolution from Lorentzian to a power-law shape with the characteristic exponent close to 1 was observed for all surfaces when the transition temperature was approached. For Ni(110), the step density increased from 300K to 1150K and the average terrace area decreased about 50%. For Ag(110), the step density increased 50% along both directions from 300K to 650K and the average terrace area decreased about 60%. We found a strong step proliferation on all surfaces near the transition temperatures which support our observation of a roughening transition. For

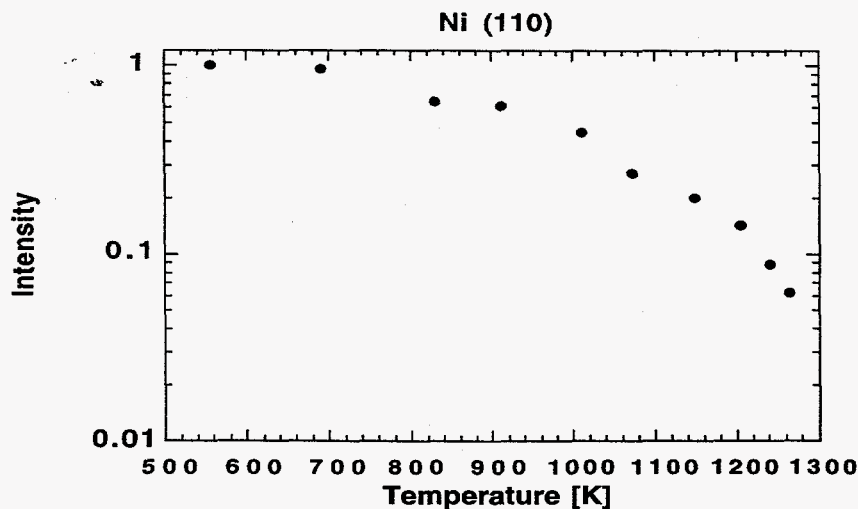


Figure 2. Integrated intensity of the (00) for Ni(110) vs temperature (along the (001)).

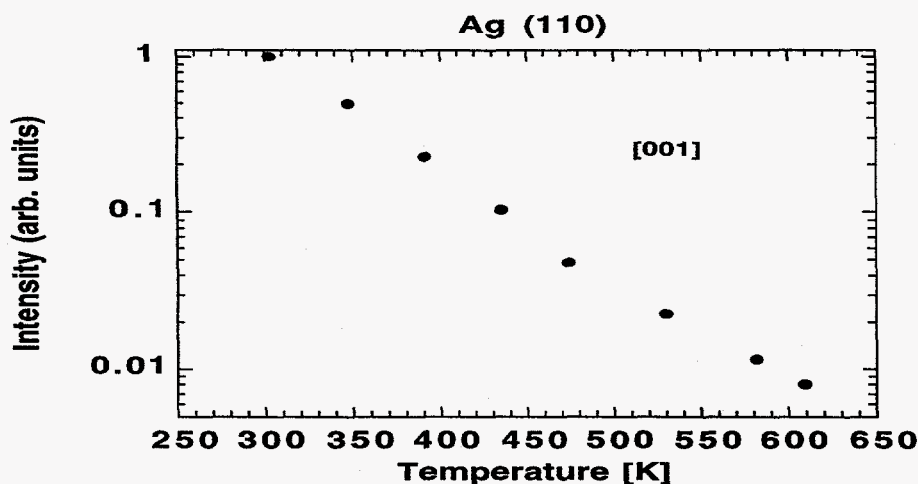


Figure 3. Integrated intensity of the (00) for Ag (110) vs temperature (along the (001)).

Ni(110), we have also studied the roughening transition with sulfur impurities on the surface. The result showed that the roughening transition temperature was very sensitive to impurities on the surface. The impurities lowered the transition temperature of the surface to 1200K. For clean Ni(110) we observed a roughening transition around 1300K, for Ag (110) the transition temperature is close to 730 K.

STM experiments were performed to corroborate the HRLEED results at room temperature. Steps and terraces were observed on the surfaces. We found the steps on the surfaces were mainly monatomic at room temperature. The terrace widths were estimated from a large amount of STM images for all three surfaces and they agreed very well with HRLEED results at room temperature. We have found strong evidence of a roughening transition taking place on the three surfaces with transition temperatures around 1000K, 1300K and 730K for Cu(110), Ni(110) and Ag(110), respectively.

CONCLUSION

We have thoroughly investigated the surface roughening transition on fcc metal Cu(110), Ni(110) and Ag(110) surfaces. We found strong evidence of a roughening transition taking place on the three surfaces with transition temperatures around 1000K, 1300K and 730K for Cu(110), Ni(110) and Ag(110), respectively. In addition, we have also studied the step distributions on these surfaces as a function of temperature. Based on the experimental data and random probability model, the step distributions and average terrace areas were calculated at several temperatures. Our research has also shown that HRLEED is a very powerful tool to study surface roughening transition.

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REFERENCES

- [1] W.K. Burton, N. Cabrera and Frank, Philos. Trans. R. Soc. London, A 243 (1951)299
- [2] Jean Lapujoulade, Surface Science Reports, 20 (1994) 191
- [3] A. Trayanov, A.C. Levi and E. Tosatti, Surf. Sci. 223 (1990)184
- [4] J.Villain, D.R. Grampel, and J. Lapujoulade, J. Phys. F,15, 809(1985)
- [5] M. den Nijs, E.K. Riedel, E.H.Conrad and T. Engel, Phys. Rev. Lett. 55, 1689 (1985) and 57, 1279 (E) (1986)
- [6] J. Lapujoulade, J. Perreau and A. Kara, Surf. Sci. 129 (1983)
- [7] F.Fabre, D. Gorse, B. Salanon and J. Lapujoulade, Phys. (Paris) 48, 1017 (1987)
- [8] K.S. Liang, E.B.Sirota, K.L. D' Amico, G.J. Hughes and S.K. Sinha, Phys. Rev. Lett. 59, 2447 (1987)
- [9] E.H. Conrad, R.M. Aten, D.S. Kaufman, L.R. Allan and T. Engel, J. Chem. Phys. 84, 1015 (1986); E.H. Conreld, L.R.Allen, D.L. Blanchard and T.Engel, Surf. Sci. 187 (1987)
- [10] G.A. Held, J.L. Jordan-Sweet, and P.M. Horn, Phys. Rev. Lett. 59, 2075 (1987)
- [11] S.G.J. Mochrie, Phys. Rev. Lett. 59 (1987) 304
- [12] M.J. Ashwin and D.P.Woodruff, Surf. Sci. 237(1990)108
- [13] R. Spitzl, H.Niehus, B. Poelsema and G. Comsa, Surf. Sci. 239(1990)243
- [14] L.H. Tjeng, M.B.J.Meinders and G.A.Sawatzky, Surf. Sci. 233(1990) 163
- [15] P. Zeppenfeld, K. Kern, R.David and G. Comsa, Phys. Rev. Lett. 62 (1989)
- [16] J. Merikoski, H. Hakkinen, M. Manninen J. Timonen and K. Kaski, Phy. Rev. B, 4938(1994)
- [17] G. Bracco, C. Malo, C.J.Moses and R. Tatarek, Surf. Sci. 287 (1993) 871
- [18] Da-Zhong Liao, Y. Cao and P. A. Montano, MRS Proceedings 208, 35 (1991).
- [19] G. Ertl and J. Koppers in "Low Energy Electrons and Surface Chemistry"
- [20] M. Henzler, Appl. Phys. A 34. 205(1984)
- [21] M. Henzler, Surf. Sci. 73(1978)240
- [22] G.-C Wang and M.B. Lagally, Surf. Sci. 81(1979)69
- [23] N.Kasupke and M.Henzler, Surf. Sci. 92(1980)407
- [24] M.G. Lagally, Surf. Sci. 13, (1982), 26
- [25] T.-M. Lu and M.G.Lagally, Surf. Sci. 120(1982)47