

Positron Tunneling and Emission from Pseudomorphically Grown Ni Films on Cu Substrates

David W. Gidley

Department of Physics, University of Michigan, Ann Arbor, Michigan 48109

(Received 27 June 1988)

The use of positrons to probe thin-film pseudomorphism is presented. The first use of reemitted-positron spectroscopy to determine critical thicknesses, volume expansions, and residual lattice strains for epitaxial Ni films on Cu(100), (110), and (111) substrates is explored. The effects of the substrate surface orientation and annealing of the film are systematically investigated. The positron deformation potential of Ni, which calibrates the spectroscopy, is separately determined by thermal expansion and by pseudomorphic expansion. The two results agree but are inconsistent with theory.

PACS numbers: 68.55.Jk, 68.35.Rh, 71.60.+z

There is a great deal of interest in understanding the epitaxial growth of thin-film overlayers that strain to conform (up to some critical thickness) with the lattice spacing of a crystalline substrate.¹ Such pseudomorphic growth affects the magnetic characteristics of ferromagnetic films² and the stability of periodic multilayer systems.³ In this Letter, the first use of positron emission⁴ from, and tunneling through, thin pseudomorphic Ni films deposited on low-index faces of Cu substrates is described. Using the technique of reemitted-positron spectroscopy (RPS)⁵ the energy and rate of reemitted positrons from a Ni-on-Cu sample is compared with positron spectra of the respective bulk samples. Strained growth of the Ni overlayer coherent with the Cu substrate (the bulk lattice mismatch is 2.57%) produces a volume expansion, or dilatation $\Delta V/V$, with respect to bulk Ni which results in an energy shift of the positron state in the Ni film. The positron deformation potential $E_d^+ = V \partial E / \partial V$, which we determine separately in a thermal expansion experiment,⁶ calibrates the volume expansion for an observed energy shift of the Ni peak in the RPS spectrum. To our knowledge, this technique is the only direct probe of *volume* deformation in thin films. It is one of the few techniques⁷ that is sensitive to lattice strain normal to the film's surface. Subsequent energy shifts in the positron state as the Cu-supported Ni film undergoes a coherent-incoherent transition at a critical thickness abruptly alter the characteristics of positron tunneling through the film from the Cu substrate. As a result, the critical thickness, h_c , for strained, coherent growth (above which misfit dislocations absorb most of the strain energy) can be observed in most cases along with the residual strain in the lattice.

Under a variety of sample preparation conditions we have attempted to determine, or set limits on, critical thicknesses, the pseudomorphic volume expansion, and the residual lattice strain for Ni films on Cu(100), (110), and (111). In addition, positron energy-level shifts induced by pseudomorphic expansion can be used with simple elastic theory to independently determine the positron deformation potential of Ni without the

temperature-dependent ambiguities^{6,8} of the thermal expansion technique. The two methods yield values of E_d^+ that are in agreement, but are 50% larger in magnitude than recent theoretical predictions.^{8,9}

The technique of RPS was presented in Ref. 5. The energy spectrum of positrons reemitted from a multilayer target in which the positrons have been implanted and thermalized is measured. Peaks appear in this spectrum corresponding to positrons that have thermalized in different material layers. The peak energy is dependent upon the sum of the electron and positron chemical potentials ($\mu^- + \mu^+$) of the material in which the positron thermalizes and is therefore independent of surface contamination or overlayer coverage. The key feature for the present work is that the peak depends sensitively on sample temperature. It is assumed⁶ that this dependence is due almost entirely to thermal *volume* expansion (i.e., lattice vibration can be neglected). Thus a shift in the peak energy from the bulk position indicates deformation, or strain, in the lattice volume. The energy shift per unit volume dilatation is given by E_d^+ .

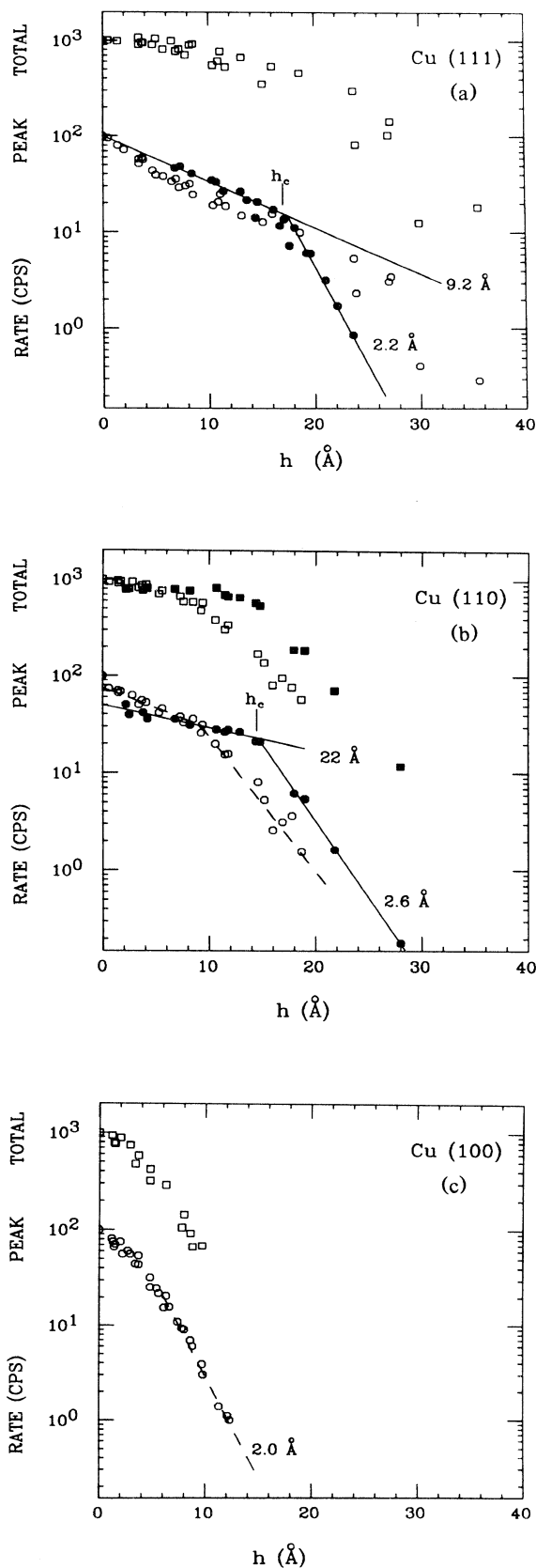
All sample preparation and RPS measurements are performed in a UHV surface analysis chamber. Thick (1–2 mm), well oriented (1°), Cu crystal substrates are cleaned by cyclic sputtering and annealing. Ni is evaporated onto the room-temperature substrates at a rate of 1–10 Å/min (and pressure $\leq 10^{-9}$ Torr) using a Ni foil-wrapped W filament. The only observed contaminant, CO, ranged from less than 1% to a maximum of 5%, depending on the condition of the evaporator. Epitaxial growth is monitored by LEED and the Ni overlayer thickness is determined by quantitative analysis of the Auger peak ratios.¹⁰ An overall systematic error of $\pm 20\%$ is estimated for all length scales determined in this fashion. The RPS spectrum and the total yield of reemitted positrons are measured as a function of Ni film thickness at room temperature either with or without a preceding flash anneal to 200°C. Since annealing produced no change in the Auger ratios for Ni-Cu(100) and Ni-Cu(111) and side-by-side Ni evaporations on these crystals produced the same Auger ratios, we assume the

growth is effectively layer-by-layer without interdiffusion alloying. Annealing reduces the apparent Ni thickness on Cu(110) and will be discussed later. Most of the data are acquired at an incident positron beam energy of 4 keV (mean implantation depth¹¹ in Cu of $\sim 400\text{-}\text{\AA} \gg$ Ni film thickness). A beam energy of 1 keV (mean depth $\sim 50\text{ \AA}$) was used to emphasize reemission from the film itself.

For RPS spectra acquired with bulk crystal targets of Ni or Cu, the Ni peak is 520 ± 10 meV higher in energy than the Cu peak.⁵ Thus an unstrained Ni overlayer presents a barrier against reemission for thermalized positrons in the Cu substrate. Any reemission would require tunneling through this barrier. However, pseudomorphic growth of a Ni film coherent with the Cu substrate lattice produces a Ni lattice expanded by 2.57% in the surface plane that should be accompanied with a concomitant contraction in the surface normal direction, which depends on the crystal orientation. Using the elastic constants of bulk Ni,¹² the pseudomorphically strained volume expansion, $\Delta V/V$, of the film is calculated to be 2.2%, 3.45%, and 3.75% for Ni on Cu(100), (110), and (111), respectively. The predicted positron energy-level shifts in the strained Ni are then $E_d^+ \Delta V/V$. We have measured E_d^+ for Ni (and also Cu) using the thermal expansion technique⁶ in the temperature range 20–350 °C. We find $E_d^+(\text{Ni}) = -15.5 \pm 0.3$ eV and $E_d^+(\text{Cu}) = -14.5 \pm 0.3$ eV. Converting the calculated values of $\Delta V/V$ into energy shifts yields -0.34 , -0.54 , and -0.58 eV, respectively. Thus the Ni barrier on the Cu(100) surface is predicted to be reduced from 0.52 to 0.18 eV, but no barrier at all is expected for Ni on Cu(110) and Cu(111).

The total rate of reemitted positrons and the Cu peak counting rate measured on all three surfaces are shown in Fig. 1 as functions of the Ni film thickness h . The Ni-Cu(111) and Ni-Cu(110) data are similar in that the peak rate initially drops with a slow exponential decay constant of $\lambda = 10\text{--}20\text{ \AA}$, which then abruptly drops to about 2.2–2.6 Å. We identify the knee in these curves as the critical thickness h_c at which lattice strain is largely relieved by misfit dislocations and thus it is the thickness at which the Ni film reverts to being a bulklike barrier. The values of λ for $h < h_c$ should be associated with the mean free path for scattering and defect trapping of a

FIG. 1. The Cu peak rate (circles) and the total positron yield (squares) (normalized to 100 and 1000 cps, respectively, at $h=0$) are shown as functions of the Ni film thickness h on three different Cu surfaces. Data for 200 °C annealed films are shown with solid symbols; unannealed data with open symbols. Critical thicknesses h_c and exponential decay constants are indicated for the straight lines drawn to guide the eye. Scatter in the data is mainly attributed to variations in the evaporator-produced CO contamination (0–5%) between different sets of data runs.



0.02–0.06-eV positron in the strained Ni film. In this regime λ is much too large to be attributable to barrier tunneling. The transmission probability for tunneling through a one-dimensional potential barrier asymptotically approaches exponential decay with $\lambda = \hbar / [8m(V-E)]^{1/2}$, where V is the barrier height and E is the positron energy. For $\lambda \geq 10 \text{ \AA}$, $V-E \leq 0.01 \text{ eV}$, or effectively no barrier at all for Ni on Cu(110) and Cu(111). However, on the Cu(100) surface the decay of the peak and total counting rates in Fig. 1 is much more rapid. No clear value of h_c is evident as λ gradually changes from roughly 4 \AA at low h to about 2 \AA at $h \approx 10 \text{ \AA}$. This latter value of λ corresponds to a Ni barrier of about 0.25 eV , close to the predicted value of 0.18 eV for strained Ni(100). Thus, consistent with our simple energy-shift predictions [using the measured value of $E_d^+(\text{Ni})$], barrier tunneling is observed for strained Ni(100) and no barrier is observed for $h < h_c$ for strained Ni(110) and Ni(111).

Figure 2 shows RPS spectra acquired for 200°C annealed Ni-Cu(111) films with $h_c \approx 15 \text{ \AA}$ (beam energy 1 keV). Only the Cu peak is present at $h < h_c$ whereas a Ni peak (or a peak within 50 meV of Ni) emerges at $h > h_c$ and becomes more pronounced as the film thickness grows. The appearance of a Ni peak that coincides with the onset of misfit dislocations—the attendant relief of strain—and the resulting onset of a Ni barrier at or near the bulk Ni energy is clearly consistent with the assignment of the knee in Fig. 1 as h_c . Similarly, for the unannealed (111) films a Ni peak appears in these data only at $h \geq 30 \text{ \AA}$. Close inspection of Fig. 1 shows that these points are well below the exponential line, consistent with $h_c \approx 25 \text{ \AA}$. For Ni-Cu(100), where no obvious value of h_c is evident from Fig. 1, the RPS spectra indicate the onset of a Ni peak for $h > 9 \text{ \AA}$. We thus conclude that $h_c \leq 9 \text{ \AA}$ for this surface.

The strained (energy shifted) Ni peak ($h < h_c$) is not resolvable from the Cu peak using the present energy analyzer because of the peak's low relative intensity (few positrons thermalize in the thin Ni overlayer) and its close proximity to the Cu peak. However, for Ni-Cu(111), where the thickest pseudomorphic films can be grown, the Cu peak always shifted $\sim 50 \text{ meV}$ downwards in energy for $h \approx h_c$ (see Fig. 2). Presumably the peak position is pulled by the pseudomorphic Ni peak located at least 50 meV below (i.e., shifted by at least $0.52 + 0.05 = 0.57 \text{ eV}$ from the bulk Ni energy). Assuming only that the strain-induced volume expansion is 3.75% for Ni on Cu(111), the lower limit of -0.57 eV on the energy shift implies $E_d^+ < -15.2 \text{ eV}$ for Ni at room temperature (the temperature dependence of E_d^+ is expected to be very small¹³). This result is in excellent agreement with our independent result, $-15.5 \pm 0.3 \text{ eV}$, using thermal expansion. It supports, without temperature-dependent ambiguities, the apparent trend^{8,9} that theoretical calculations of E_d^+ can only account for

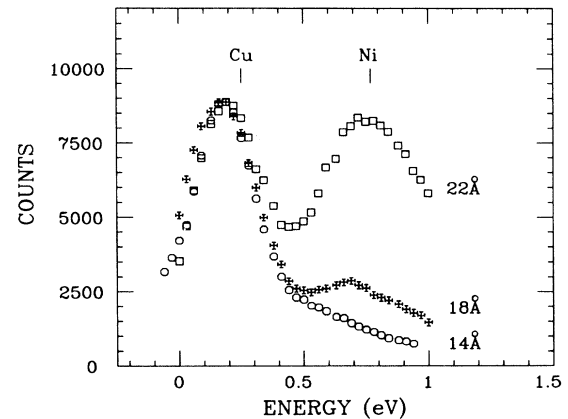


FIG. 2. RPS spectra acquired at 1-keV positron beam energy for three different thicknesses of 200°C annealed Ni films on Cu(111). Data have been normalized to the Cu peak height. The strained Ni peak for $h = 14 \text{ \AA}$ is presumably unresolved from the Cu peak. A bulklike Ni peak appears for $h > h_c$ ($h_c \approx 15 \text{ \AA}$) but no intermediate peak indicative of any residual lattice strain is observed.

about $\frac{2}{3}$ of the magnitude of E_d^+ .

The preliminary RPS results for pseudomorphic Ni films are summarized as follows.

(1) For 200°C annealed Ni films on Cu(111) and Cu(110) $h_c \sim 15 \text{ \AA}$. For unannealed films $h_c = 10 \text{ \AA}$ on Ni-Cu(110), $h_c \sim 25 \text{ \AA}$ on Ni-Cu(111), and $h_c \leq 9 \text{ \AA}$ on Ni-Cu(100). Previous transmission electron microscope (TEM) studies indicate $h_c = 14.6 \pm 3 \text{ \AA}$ for Ni-Cu(100) (80°C anneal),¹⁴ and $h_c \approx 10 \text{ \AA}$ for Cu(111) (200°C anneal).¹⁵ Naively, and contrary to our observations, Ni-Cu(111) should have the lowest h_c since it has the most highly deformed lattice volume [3.75% vs 2.2% for Ni-Cu(100)]. However, the type and generating processes of misfit dislocations, along with processes that impede dislocation formation, are highly dependent on the geometry of the film and its substrate interface.^{1,16} Calculations¹⁷ suggest that the hexagonal fcc(111) interface is more stable than corresponding rectangular interfaces. Detailed consideration of these effects on h_c is beyond the scope of this Letter. The unexpected increase in h_c with annealing for Ni-Cu(110) should be taken cautiously since the Auger analysis indicated that annealing to 200°C produced either interdiffusion alloying or a change in growth mode on this open face. Alloying at the interface is expected to relieve strain and effectively increase h_c .¹⁸ In addition, top-layer contraction of the Cu(110) [and Ni(110)] surface is very large ($\sim 10\%$)¹⁹ and such reconstruction may affect pseudomorphic film growth.

(2) Critical thicknesses depended not only on annealing temperature but also on the presence of contaminants in the evaporation-deposition process and on the surface preparation of the Cu substrate. Carbon and ox-

gen contamination may have inhibited misfit dislocation formation since we observed a tendency for h_c to increase ~ 2 Å for runs in which the CO contamination approached 5%. On two specially prepared Cu(110) and Cu(111) substrates that were overheated and recrystallized in a complicated, unrecognizable orientation we observed smaller values of h_c by 50% or more. Thus, there should be further study of the sensitivity of pseudomorphic growth parameters to different methods of Cu substrate preparation (e.g., compare our sputtered and annealed Cu crystals to the TEM thin Cu films vapor deposited on NaCl).

(3) For well-ordered Cu(100) and Cu(111) substrates and clean Ni depositions no indication of residual lattice strain is observed for $h > h_c$. This contradicts elastic theories²⁰ and TEM observations^{14,15} which indicate that the strain should drop smoothly (approximately as $1/h$) for $h > h_c$. We do not detect (at the 50-meV level) any Ni peaks intermediate between the strained Ni peak and the bulk peak that would indicate a partially strained lattice (e.g., see Fig. 2). For $h > h_c$, the bulk peak simply grows in intensity with h indicating that more positrons are stopping in the Ni overlayer and/or that some regions of the film undergo the coherent-incoherent transition at different average h due to local thickness nonuniformities. For the recrystallized substrates mentioned above (which have lower values of h_c) intermediate peaks are observed and the residual lattice strain so deduced does follow a roughly $1/h$ dependence. Thus RPS can be sensitive to the effect. Future work should concentrate on resolving this apparent discrepancy with previous research.

The above results demonstrate the sensitivity of RPS to the dependence of misfit dislocation formation on the crystal face and the surface roughness and defect nature of the substrate, as well as the annealing temperature of the film. This dependence presents some problems in interpreting TEM results because the Cu substrates are, by necessity, evaporated films (with more defects than single crystals) and in some cases, the Ni film is exposed to air and work hardening (in removing the support substrate) prior to analysis in the TEM.²¹ TEM images offer the advantage of direct imaging of misfit dislocations and hence a determination of the orientation and type of dislocation formed. However, given the difficulties of sample preparation,²¹ positron studies might serve as an important check on their results. RPS can provide highly quantitative measurements of h_c and strain in thin films with *in situ* sample preparation and nondestructive analysis procedures. Future applications of RPS to pseudomorphic growth should include further tests for residual strain above h_c and the substrate surface roughness tests mentioned earlier. Interdiffusion alloying at the Cu-Ni interface as a means of stabilizing the pseudomorphically strained film¹⁸ could be investigated. Compressive film strain²² and other tensile strain cases are feasible. Further cataloging of RPS peak posi-

tions⁵ and measurements⁶ of E_d^+ would facilitate selection of candidate materials.

I thank W. E. Frieze, T. W. Capehart, B. D. Wissman, and members of the Michigan positron group for helpful discussions and technical assistance. I am especially indebted to S. P. Mohlke who performed the thermal expansion measurements and assisted me throughout the experiment. This work is supported by the National Science Foundation (Grant No. DMR-8618721) and the Office of the Vice President for Research of the University of Michigan.

¹See, for example, R. Bruinsma and A. Zangwill, *J. Phys. (Paris)* **47**, 2055 (1986); J. W. Matthews, *Epitaxial Growth* (Academic, New York, 1975).

²U. Gradmann, *Appl. Phys.* **3**, 161 (1974); M. A. Thompson and J. L. Erskine, *Phys. Rev. B* **31**, 6832 (1985), and references therein.

³E. Bauer and J. H. van der Merwe, *Phys. Rev. B* **33**, 3657 (1986); D. Ariosa *et al.*, *Phys. Rev. B* **37**, 2415 (1988).

⁴For a review of thin-film positron studies see P. T. Schultz and K. G. Lynn, *Rev. Mod. Phys.* **60**, 701 (1988).

⁵D. W. Gidley and W. E. Frieze, *Phys. Rev. Lett.* **60**, 1193 (1988).

⁶E. M. Gullikson and A. P. Mills, Jr., *Phys. Rev. B* **35**, 8759 (1987).

⁷S. A. Chambers *et al.*, *Phys. Rev. B* **33**, 8810 (1986); Y. Kuk, L. C. Feldman, and P. J. Silverman, *Phys. Rev. Lett.* **50**, 511 (1983).

⁸O. V. Boev, M. J. Puska, and R. M. Nieminen, *Phys. Rev. B* **36**, 7786 (1987). Note that the procedure in this reference for determining experimental E_d^+ values from referenced experiments is not correct.

⁹M. Farjam and H. B. Shore, *Phys. Rev. B* **36**, 5089 (1987).

¹⁰Mean free paths of the 848- and 920-eV Auger electrons in Ni are taken to be 10.1 and 10.6 Å, respectively, from D. R. Penn, *J. Electron Spectrosc.* **9**, 29 (1976).

¹¹A. Vehanen, *Appl. Phys. A* **43**, 269 (1987).

¹²G. A. Alers *et al.*, *J. Phys. Chem. Solids* **13**, 40 (1960).

¹³C. Herring and M. H. Nichols, *Rev. Mod. Phys.* **21**, 185 (1949).

¹⁴J. W. Matthews and J. L. Crawford, *Thin Solid Films* **5**, 187 (1970).

¹⁵U. Gradmann, *Ann. Phys. (Leipzig)* **7**, 213 (1964); *Surf. Sci.* **13**, 498 (1969).

¹⁶J. W. Matthews, in *Dislocations in Solids*, edited by F. R. N. Nabarro (North-Holland, Amsterdam, 1979), Vol. 2, p. 461.

¹⁷J. H. van der Merwe, *Thin Solid Films* **74**, 129 (1980).

¹⁸B. W. Dodson, *Phys. Rev. B* **36**, 6288 (1987).

¹⁹H. L. Davis, J. R. Noonan, and L. H. Jenkins, *Surf. Sci.* **83**, 559 (1979).

²⁰See discussion and references in Refs. 1, 12, and 14 above.

²¹For *in situ* TEM preparation techniques see G. Honyo and K. Yagi, in *Current Topics in Materials Science*, edited by E. Kaldis (North-Holland, Amsterdam, 1980), Vol. 6.

²²Some data were acquired in Ref. 5 on the reverse system of Cu on Ni(110). However, we calculate that there is no crossover of the Cu-Ni positron states for this system and indeed no knee (and hence no value of h_c) was observable.