GPO PRICE $ _____

OTS PRICE(S) $ _____

Hard copy (HC) _____

Microfiche (MF) _____

NASA CR-54206
Brown 6017 4

NASA

EXPERIMENTAL INVESTIGATIONS IN EPITAXIAL GROWTH OF CRYSTALLINE LAYERS

by

H. E. Farnsworth, Barstow University Professor

C. A. Haque, Research Associate

prepared for

ATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Grant No. NASA NsG-418

CAT-26

Brown University, Providence, R.I.

N65-12727
(ACCESSION NUMBER)
13
(THRU)
1
(CODE)
26
(CATEGORY)
(NASA CR OR TMX OR AD NUMBER)
CR-54206
FACILITY FORM 602

NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the National Aeronautics and Space Administration (NASA), nor any person acting on behalf of NASA:

A.) Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B.) Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method or process disclosed in this report.

As used above, "person acting on behalf of NASA" includes any employee or contractor of NASA, or employee of such contractor, to the extent that such employee or contractor of NASA, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with NASA, or his employment with such contractor.

Requests for copies of this report should be referred to

National Aeronautics and Space Administration
Office of Scientific and Technical Information
Attention: AFSS-A
Washington, D.C. 20546

FINAL REPORT

EXPERIMENTAL INVESTIGATIONS IN EPITAXIAL GROWTH OF CRYSTALLINE LAYERS

by

H.E. Farnsworth, Barstow University Professor

C.A. Haque, Research Associate

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

October 31, 1964

Grant No. NASA NsG-418

Technical Management
NASA Lewis Research Center
Cleveland, Ohio
Space Power Systems Division
Solar and Chemical Power Branch
Clifford K. Swartz

BROWN UNIVERSITY
Providence, Rhode Island

EXPERIMENTAL INVESTIGATIONS IN EPITAXIAL GROWTH OF CRYSTALLINE LAYERS

by

H.E. Farnsworth and C.A. Haque

12727

ABSTRACT

Nickel is evaporated in high vacuum from a calibrated source, one monolayer at a time, on a clean (111) copper single crystal substrate. Excellent order in arrangement of condensed nickel atoms with the same orientation as the substrate, but with the lattice spacing of nickel, is observed when the substrate is maintained at about 200°C during evaporation. Each successive monolayer grows epitaxially with respect to the layer immediately below it, always with the lattice spacing of nickel. No more than three atomic layers contribute appreciably to the diffracted intensity below about 250eV. The contribution from the first layer predominates.

Author

EXPERIMENTAL INVESTIGATIONS IN EPITAXIAL GROWTH OF CRYSTALLINE LAYERS

by H.E. Farnsworth and C.A. Haque

Brown University

SUMMARY

The object of this investigation was to determine the structure of an epitaxial layer in the initial stages of one to several monolayers for the case in which the lattice spacing of the surface layer differs from that of the supporting substrate by not more than a few percent. It is known that complete coverage is obtained in the first monolayers when the lattice spacings differ by less than 0.5 percent and that clumping occurs when the spacings differ by as much as 13 percent, with the spacing of the surface layer always the same as that for the same material in bulk form. However, there are insufficient data at present over a wide range of variables and under extreme conditions of cleanliness to formulate a general theory of epitaxy. It is known that one monolayer of surface contamination can alter the nature of epitaxial growth. Hence, it is essential to use ultra high vacuum techniques to eliminate spurious effects of contamination and to obtain an atomically clean surface initially on which to deposit the epitaxial layer. The method must be capable of determining the structure of a single monolayer. The low energy electron diffraction technique satisfies this requirement and is used in the present investigation. The materials selected were nickel and copper, since they have the same lattice structure and their lattice spacings differ by about 2.8 percent. A nickel film was deposited from the vapor onto a (111) copper crystal surface since the spacing of nickel is less than that of copper.

In addition to the above objective, it was possible to obtain valuable information on the depth of penetration of diffracted electrons in the case of nickel. It was found that at room temperature nickel formed in ordered as well as disordered structure without complete coverage of copper, thus indicating clumping. With the copper at 200°C excellent order and coverage was obtained with one or more monolayers. The lattice formed by the nickel atoms was the same as that of bulk nickel and had the orientation of the copper. Thus, under these conditions it was possible to obtain uniform coverage without clumping even though the lattice constants differ by 2.8 percent. Further tests with other materials may help in determining the maximum misfit without clumping. Since the type of atoms involved is also a determining factor, tests should be made on different combinations of materials having misfits of the same magnitude.

Observations on nickel deposits of one to several monolayers show that the first monolayer predominates in its contribution to the diffraction pattern and that contributions from more than three monolayers are insignificant in the range below 250V.

INTRODUCTION

Because initial epitaxial growth has been shown to be sensitive to small amounts of contamination[1], it is important to determine the conditions which govern this growth under ultra high vacuum conditions. In addition, a method of structure determination must be used which can be applied to a single monolayer. It has been shown that the low energy electron diffraction (LEED) technique satisfies this requirement[1,2]. Using this technique, it was found that complete coverage is obtained at room temperature when the epitaxial layer has essentially the same lattice constant as that of the substrate, as in the case of silver on gold, where the lattice constants differ by only about 0.4 percent[2]. However, in the case of copper on titanium[1], for which the lattice spacings differ by about 13 percent, clumping of copper occurs in the initial stages of deposit. Although the orientation of the copper crystallites is determined by that of the substrate, the spacing is always the same as the normal copper spacing. It is, therefore, important to determine the degree of misfit and other relevant conditions which are required to produce a clumping or nonclumping of the epitaxial layer in the initial stages of one monolayer or less.

This type of investigation also furnishes information on the number of atomic layers contributing to the electron diffraction pattern. This information is of value in the interpretation of the intensity distribution of the diffraction pattern.

In the present investigation, a nickel film has been deposited on a copper substrate. For this combination the lattices are both face centered cubic, but the nickel spacing is about 2.8 percent smaller than that of copper.

The characteristic intensity distribution of diffracted beams was obtained as a function of the voltage of incident low energy electrons for an atomically clean surface of Cu(111). Nickel was evaporated from a calibrated source, one monolayer at a time, on the atomically clean surface of Cu(111), and immediate LEED observations were made of the nickel-copper surface.

The results reported here concern:

(a) the growth and structure of nickel thin films on a Cu(111) substrate;

(b) the penetration of electrons in a nickel-copper system as a function of the energy of the incident electrons.

EXPERIMENTAL PROCEDURE AND RESULTS

The nickel film was deposited from the vapor obtained by heating a high purity nickel slug below the melting point in ultra high vacuum. A tungsten filament was mounted behind the nickel slug to permit heating by electron bombardment. A molybdenum box enclosed the filament and nickel slug with a 2mm opening opposite the front face of the slug and at a distance of 3mm. One end of a Pt - Pt 13 percent Rh thermocouple was imbedded in one side of the nickel slug. This geometry of the evaporator ensured a uniform rate of evaporation from unit area of the flat nickel face.

The calibration of the evaporator was made in an auxiliary vacuum system in which nickel was deposited from the vapor onto 18mm x 18mm flat glass microscope slides. The residual ambient pressure during evaporation was 5×10^{-8} Torr. Careful cleaning procedures[3] were used for the slides. Blank slides, on which no deposits were made, were used to check on outgassing and other effects that would cause errors when the weights of the deposits of nickel were evaluated. All slides were weighed initially prior to evaporation and after nickel deposition in a Mettler's micro-balance with a sensitivity of 1 μgm. The weights deposited were 10 μgms and above, and were recorded as a function of the time of evaporation, at a fixed temperature of 1204°C of the nickel slug. This temperature of 1204°C was selected after previous tests in which nickel was evaporated at different temperatures. The time required to deposit one monolayer of nickel was 14 minutes. This was determined by extrapolating the linear relationship between time and weight of deposit at the evaporating temperature of 1204°C.

The Cu(111) single crystal was mechanically polished and etched chemically in a solution of 32 percent HNO_3 at 70°C. X-ray diffraction patterns were subsequently observed to confirm the (111) orientation, prior to inserting the crystal in the diffraction tube.

A sketch of the diffraction tube, block diagram of the entire experimental system and the experimental procedures are delineated elsewhere[4]. The only addition being the calibrated nickel evaporator which was inserted as a side arm so that the direction of deposit was 30° from the normal to the crystal surface. Vacuum techniques for obtaining pressures around 2×10^{-10} Torr were used. During the calibration of the nickel evaporator, each glass slide was placed 5cm from the evaporating surface. This distance was maintained for the Cu(111) whenever it was subjected to nickel evaporation. The evaporator assembly was well outgassed and the evaporating surface was always maintained at the operating temperature of 1204°C for sometime, before exposing the Cu(111) crystal to nickel evaporation.

The Cu(111) crystal was subjected to LEED investigations at a pressure of 5×10^{-10} Torr. Initially, no sharp beams were observed. The crystal was slowly heated to about 800°C and on cooling it to room temperature, LEED measurements indicated the presence of characteristic diffraction beams. The crystal was then argon ion bombarded at 300V and 20 μamp for 15 minute intervals, each bombarding interval being followed by annealing at 300°C for 30 minutes. Fig. 1 shows the usual colatitude angle (Θ) against primary voltage (V) and intensity (I) against V data obtained for the $\bar{1}0$ beam in the $(1\bar{1}0)$ azimuth after the above treatment. The open circles in Fig. 1 represent experimental Θ vs V points which fall well along the theoretical surface grating lines. The Cu(111) surface as such was considered atomically clean. The theoretical surface grating curves were plotted from usual calculations[4], for a lattice constant a = 3.61 A for copper.

When a monolayer of nickel was evaporated from the calibrated source, on the clean surface of Cu(111) at room temperature and at a pressure of 2×10^{-8} Torr, immediate LEED investigations of the surface indicated ordered as well as disordered condensation of the monolayer of nickel atoms. Some diffracted beams had sharp peaks with nickel spacings, some were original copper beams, some were diffuse with large half-widths in wavelength and some were missing, thus indicating that complete coverage was not obtained. This was true for at least three monolayers, which was the maximum number deposited under these conditions.

Excellent order in arrangement of condensed nickel atoms with the same orientation as the substrate was observed when the substrate Cu(111) was maintained at a temperature of about 200°C. The lattice spacing was that of bulk nickel. Five monolayers of nickel were evaporated on the Cu(111) crystal, one monolayer at a time, and the intensities of the diffracted beams were recorded as a function of the primary voltage after each monolayer deposition. Each successive monolayer grows epitaxially with respect to the layer immediately below it, always with the nickel spacing.

Fig. 2 shows Θ vs V and I vs V characteristics for one monolayer of nickel on Cu(111). Similarly Fig. 3 is for two monolayers of nickel on Cu(111) and Fig. 4 for three monolayers. Fig. 5 is the I vs V characteristic for Ni(111) taken from previous work in this laboratory[5] for the $\bar{1}0$ beam.

DISCUSSION

From the I vs V data, after one monolayer of nickel was deposited with the crystal at room temperature, it appears that the nickel condenses in islands or clumps, some of which are ordered, with the same orientation as the substrate copper but with nickel spacings. The presence of beams characteristic of copper indicates regions where no nickel remains. The diffuse beams with large half-widths and the missing beams are probably due to disordered condensation.

It is seen from the theoretical surface grating curves of Fig. 2 that the resolution in V between Cu and Ni varies from 2 volts at large colatitude angles to about 12 volts at small colatitude angles. This of course is due to the small 2.8 percent mismatch in the lattice constants of Cu and Ni. The difference in V becomes more pronounced for the $\bar{2}0$ and 20 beams in the $(1\bar{1}0)$ azimuth and also for the $\bar{2}1$ beam in the $(11\bar{2})$ azimuth. The experimental points of Θ vs V plots for all these beams led to the conclusion that the epitaxial nickel film always has the nickel spacing. This is in agreement with previous observations on copper[1]. Although the concept of an epitaxial temperature appears to be characteristic of this system, this is not true in general[6].

Information on electron penetration is obtainable from a comparison of the I vs V data from Figures 4, 3 and 2 with that of Fig. 5. It is apparent that the penetration is a function of the energy of the incident electrons. The fine structure seen in Fig. 5 attributed to steps and stacking faults[5] is only partly observable

in Fig. 4. This does not mean that the nickel condenses with no defects. In this experimental setup it was not possible to sweep over all colatitude angles. Hence, it is probable that the fine structure could not always be observed.

The I vs V data of Fig. 4 obtained after three monolayers were deposited compares very well with those of Fig. 5 up to a primary voltage of 190 volts. It can be inferred from this that more than 90 percent of the diffracted electrons of energy up to 190eV come from the first three monolayers. For two monolayers, as seen in Fig. 3, the intensity curve starts to deviate from that of Fig. 4 at an incident energy of about 140eV. Most of the diffracted electrons below 140eV appear to come from the first two monolayers. Similarly, from Fig. 1, the deviation in intensity curve when compared to that in Fig. 2 begins at about 90 volts. Hence, below this value most of the diffracted electrons appear to come from the surface monolayer.

CONCLUSION

LEED is well suited for studies of the structure and growth of thin metallic films. Detailed observations of the initial growth of films of a monolayer or less by the LEED method can furnish significant information for theoretical problems concerning epitaxy.

For the Ni-Cu system, the contribution from the surface monolayer predominates in the low energy range. Between 190 and 242 volts, the difference in intensity curves indicates that there is no appreciable contribution from more than three monolayers. This information is important in an interpretation of intensity distribution data.

REFERENCES

1. R.E. Schlier and H.E. Farnsworth, J. Phys. Chem. Solids, Vol. 6, Nos. 2/3, p. 271 (1957).

2. H.E. Farnsworth, Phys. Rev., 49, 605 (1936).

3. K.H. Behrndt, Vacuum., 13, 337 (1963).

4. C.A. Haque and H.E. Farnsworth, Surf. Sci. (in press).

5. R.L. Park and H.E. Farnsworth, Proceedings of the Int. Conf. on the Phys. & Chem. of Solid Surfaces, Brown University, June 1964 (to be published in Surf. Sci.).

6. G.A. Basset, J.W. Menter and D.W. Pashley, Structure and Properties of Thin Films, 11, John Wiley, New York, (1959).

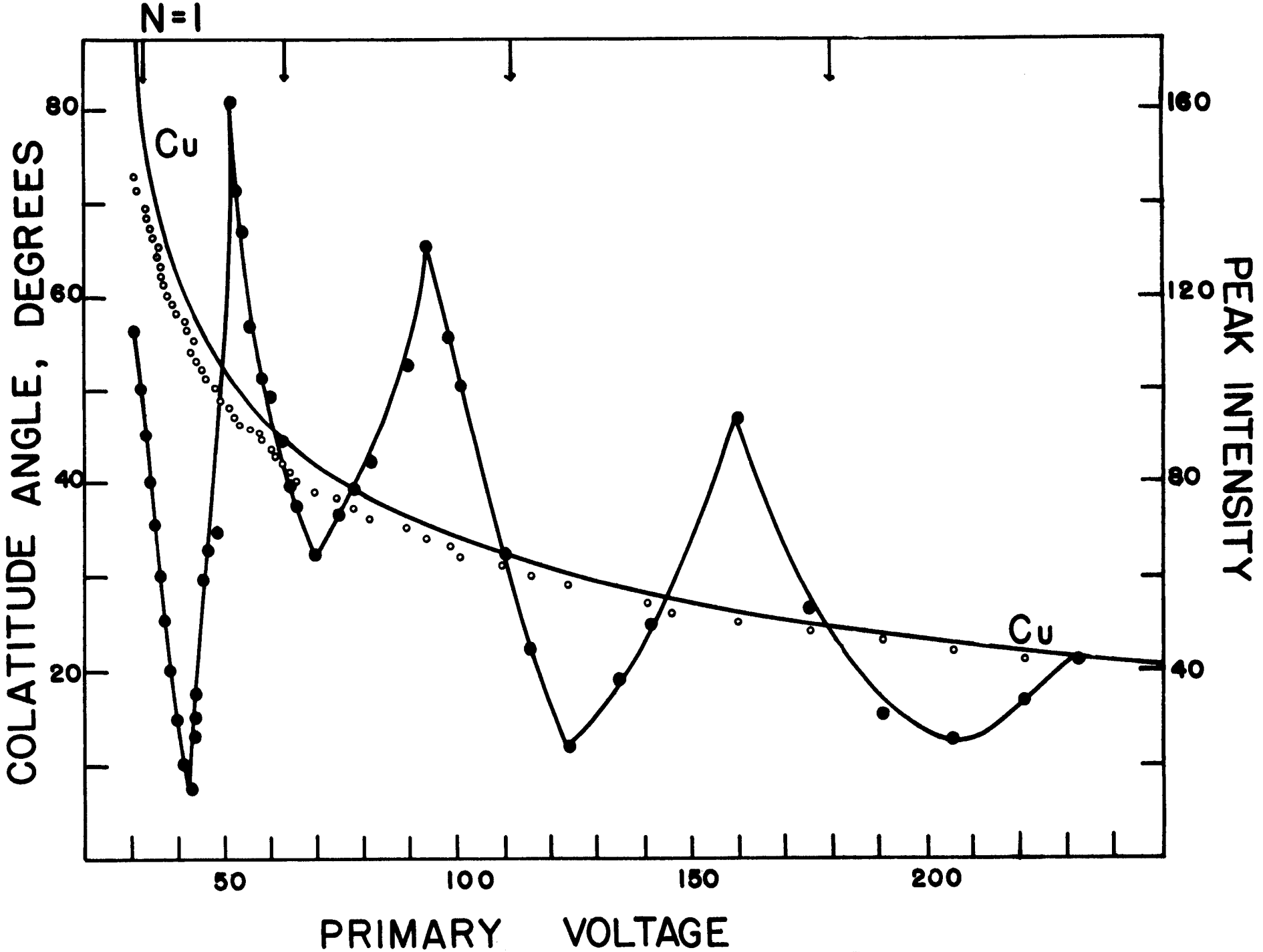

Fig. 1 Θ vs V (open circles) and I vs V (solid circles) for the I0 beam of clean Cu.

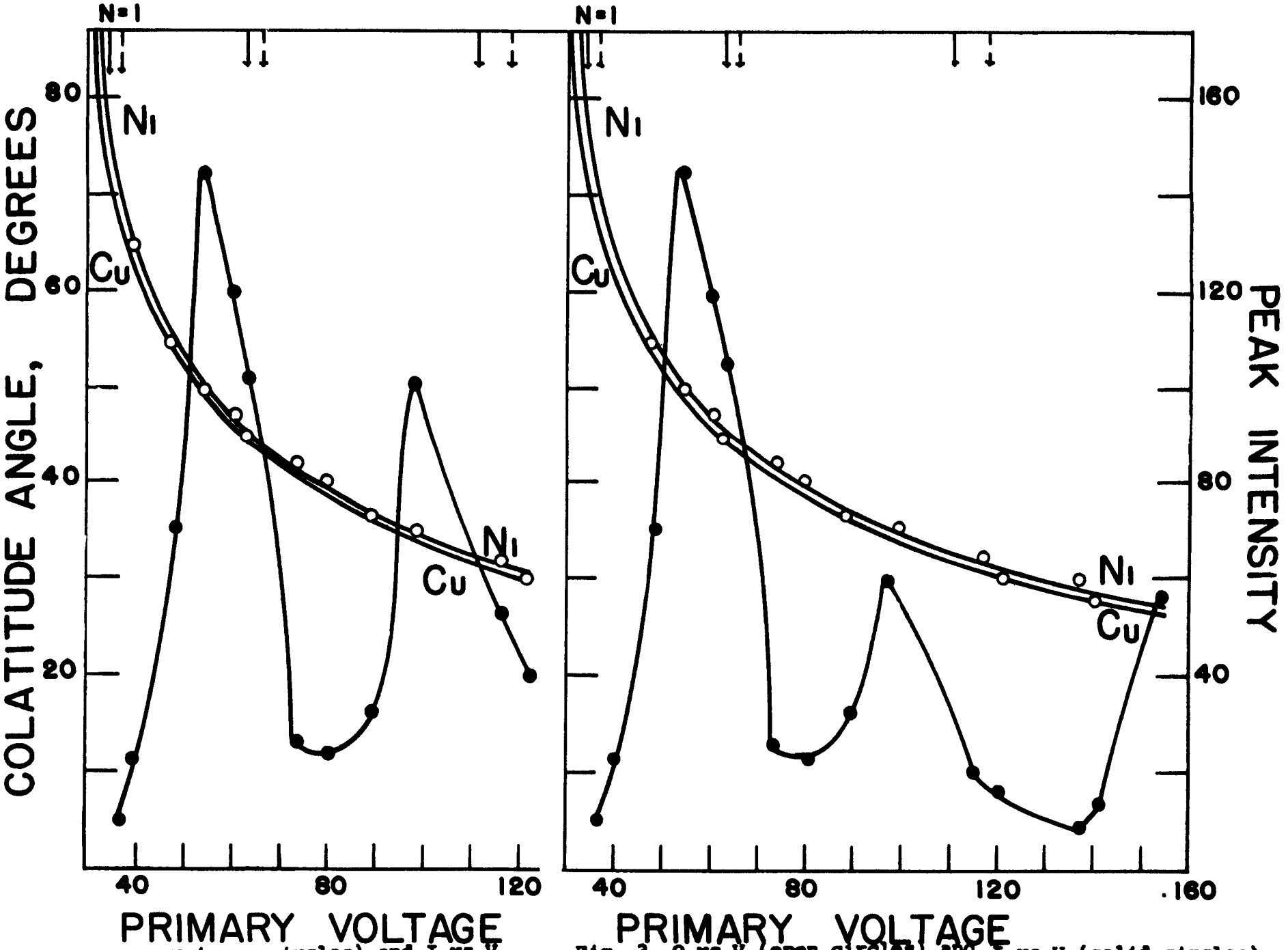

Fig. 2 θ vs V (open circles) and I vs V (solid circles) for the I0 beam for one monolayer of Ni on Cu

Fig. 3 θ vs V (open circles) and I vs V (solid circles) for the I0 beam for two monolayers of Ni on Cu.

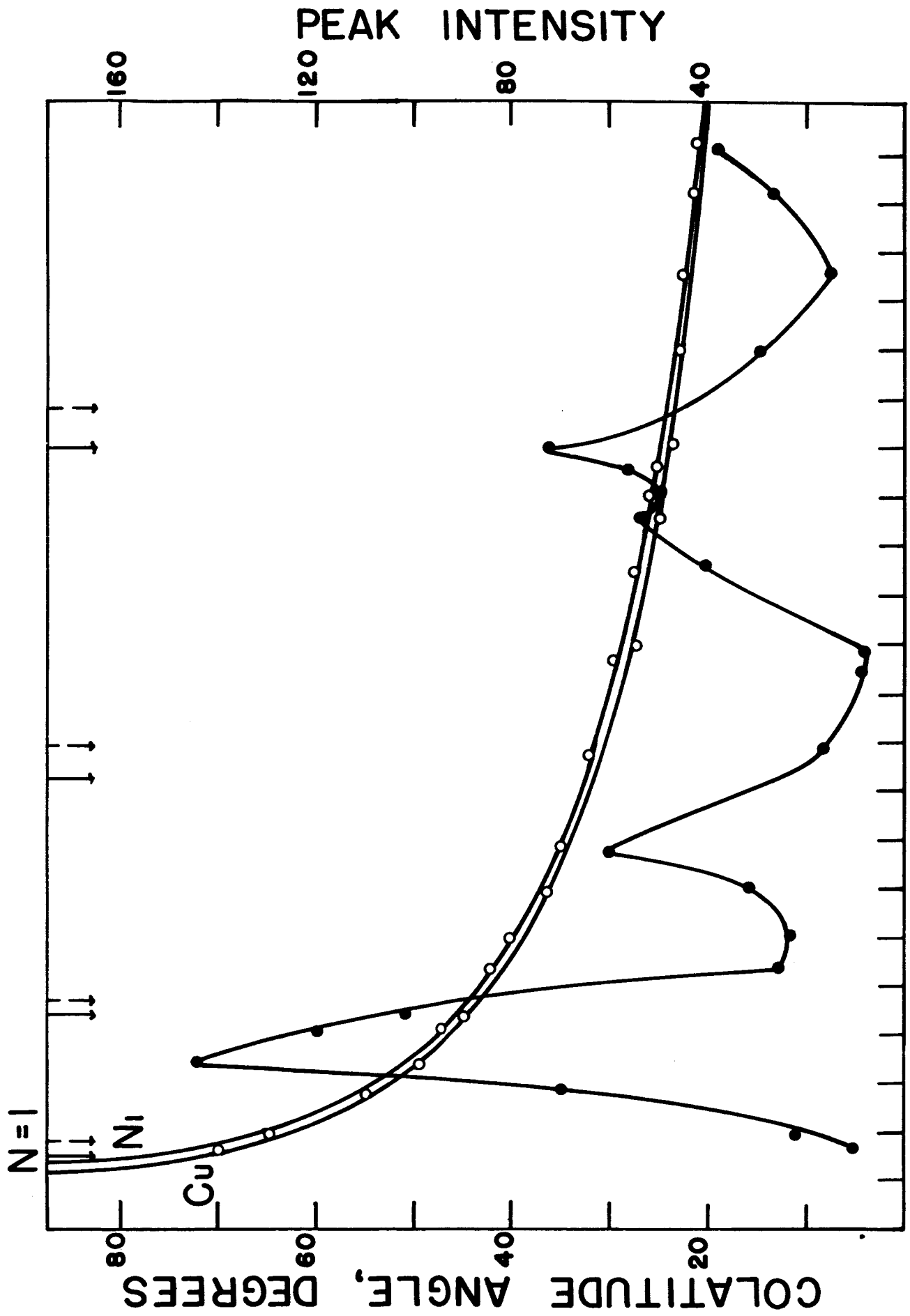

Fig. 4 θ vs V (open circles) and I vs V (solid circles) for the I0 beam for three monolayers of Ni on Cu.

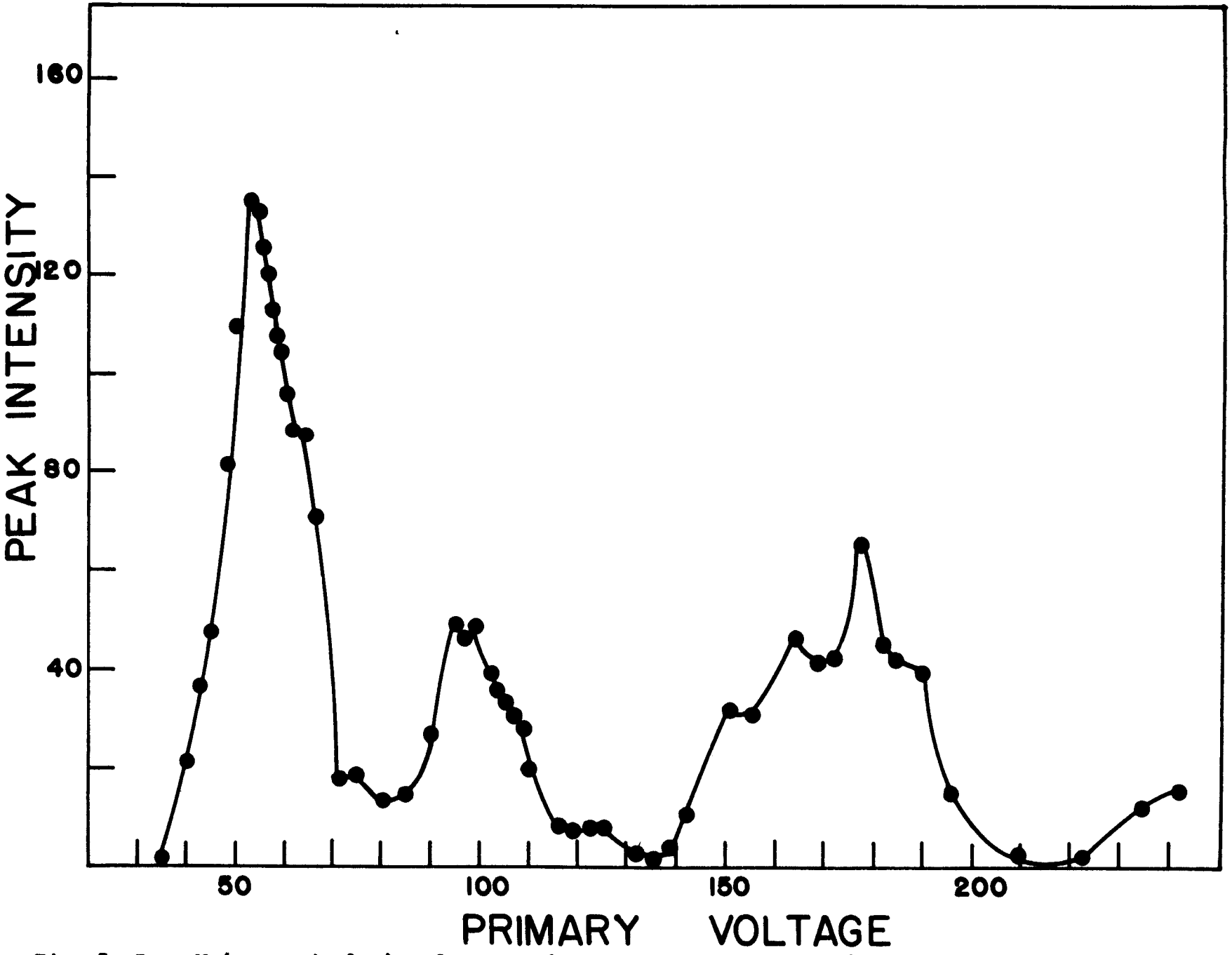

Fig. 5 I vs V (open circles) and I vs V (solid circles) for the Ī0 beam of clean Ni(111).