

# Release of compressive intrinsic stress in ultraclean thin nickel films as a result of adsorption of gases

**Citation for published version (APA):**

Janssen, M. M. P. (1969). Release of compressive intrinsic stress in ultraclean thin nickel films as a result of adsorption of gases. *Journal of Applied Physics*, 40(7), 3055-3056. <https://doi.org/10.1063/1.1658129>

**DOI:**

[10.1063/1.1658129](https://doi.org/10.1063/1.1658129)

**Document status and date:**

Published: 01/01/1969

**Document Version:**

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

**Please check the document version of this publication:**

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

**General rights**

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

[www.tue.nl/taverne](http://www.tue.nl/taverne)

**Take down policy**

If you believe that this document breaches copyright please contact us at:

[openaccess@tue.nl](mailto:openaccess@tue.nl)

providing details and we will investigate your claim.

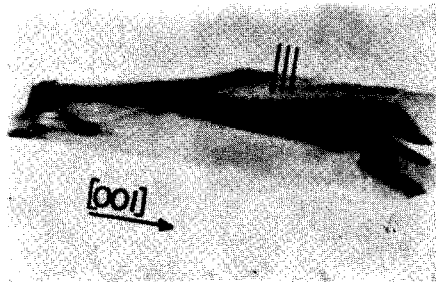


FIG. 2. A wide-beam-transmission topograph from a selenium single crystal with a 003 reflection. Dislocations of small-angle boundaries (dark in the figure) are visible at the point of the arrows. Magnification 20.



FIG. 3. A wide-beam-transmission topograph from a tellurium single crystal with a 003 reflection. Magnification 20.

tion angles between them are of the order of the turning angle 2 min. Some individual small-angle boundaries are detectable in the upper part of Fig. 1(a).

Figure 2 shows more clearly small-angle boundaries (dark areas) in a selenium crystal and the arrows indicate some dislocations from which the boundaries are formed. The dislocations are normal to the [001] direction. They are edge-type dislocations because a screw dislocation perpendicular to the  $c$  axis is invisible with a 003 reflection. The spacing of the dislocations is about  $50 \mu$ . The misorientation angle of this small-angle tilt boundary is thus about 2 sec at the point of the arrows. The misorientation angle of the uppermost curved boundary is so large that a part of the rectangularly shaped irradiated area is not at all visible.

Dislocations of the tellurium crystals are visible in Fig. 3. The contrast is, however, weaker than in Fig. 2 because the absorption coefficient times the crystal thickness is greater than unity ( $\sim 1.3$ ). The dislocations are in the same direction as in selenium. Small-angle boundaries similar to those found in the selenium samples were also observed.

These results give support to the barrier model used in the interpretation of the electrical conductivity and photoconductivity measurements of selenium.<sup>13-15</sup> The small-angle boundaries divide the crystals into cells as shown in Fig. 1. The misorientation angles of the boundaries are as a rule of the order of a few minutes.

\* Present address: Department of Physics, Brown University, Providence, Rhode Island 02192.

<sup>1</sup> D. E. Harrison, *Recent Advances in Selenium Physics*, (Pergamon Press, Inc., Ltd., London, 1965), p. 67.

<sup>2</sup> T. O. Tuomi, *Acta Polytech. Scand. Ph* **56**, 1 (1968).

<sup>3</sup> F. Eckart, *Recent Advances in Selenium Physics*, (Pergamon Press, Inc., Ltd., London, 1965), p. 85.

<sup>4</sup> J. D. Harrison and A. Sagar, *J. Appl. Phys.* **38**, 3791 (1967).

<sup>5</sup> W. Henrion and F. Eckart, *Z. Naturforsch.* **19a**, 1024 (1964).

<sup>6</sup> M. Shiojiri, *Jap. J. Appl. Phys.* **6**, 163 (1967).

<sup>7</sup> C. Griffiths and H. Sang, *Appl. Phys. Lett.* **11**, 118 (1967).

<sup>8</sup> L. C. Lovell, J. H. Wernick, and K. E. Benson, *Acta Met.* **6**, 716 (1958).

<sup>9</sup> J. S. Blakemore, J. W. Schultz, and K. C. Nomura, *J. Appl. Phys.* **13**, 2226 (1960).

<sup>10</sup> E. M. Hörl and J. Weiss, *J. Appl. Phys.* **38**, 5132 (1967).

<sup>11</sup> H. Barth and R. Hosemann, *Z. Naturforsch.* **13a**, 792 (1958).

<sup>12</sup> The authors are indebted to W. Henrion, who kindly supplied them with the selenium single crystals.

<sup>13</sup> K. Plessner, *Proc. Phys. Soc. (London)* **B64**, 671 (1951).

<sup>14</sup> J. Stuke, *Phys. Status Solidi* **6**, 441 (1964).

<sup>15</sup> T. O. Tuomi and S. O. Hemilä, *Phys. Lett.* **20**, 250 (1966).

## Release of Compressive Intrinsic Stress in Ultraclean Thin Ni Films as a Result of Adsorption of Gases\*

M. M. P. JANSSEN†

Center for Surface and Coatings Research, Lehigh University,  
Bethlehem, Pennsylvania 18015

(Received 25 November 1968; in final form 10 February 1969)

The work reported herein represents one phase of a program designed to better understand the properties of clean metals. The eventual objective of these studies is to relate this understanding to the phenomenon of stress corrosion cracking and environment-enhanced fatigue failure.

Thin nickel films were evaporated onto extremely well out-gassed soft glass or Vycor brand glass substrates at 35°C in equipment similar to that used by Neugebauer.<sup>1,2</sup> Evaporation rates varied from 5 to 10 Å/min and the vacuum during deposition was better than  $5 \times 10^{-10}$  Torr. Measurements on the films were done at room temperature in the vacuum system in which the films were prepared. The vacuum during measurement was better than  $1.5 \times 10^{-10}$  Torr. Under these vacuum conditions it is believed that no appreciable gas adsorption takes place during film preparation and measurement. Thermal stresses, associated with the small difference between deposition and measurement temperature, were neglected. Stresses in films were determined by ferromagnetic resonance (Varian V-4502 EPR spectrometer). During the measurements, the film plane was perpendicular to the main magnetic field; this arrangement yields the most accurate values of  $K_{\perp}$  is the anisotropy constant for magnetization in a direction perpendicular to the film plane. All contributions to  $K_{\perp}$ , other than isotropic stress, were neglected. This approximation is justified in view of the strong magnetoelastic coupling in Ni and the relatively high stress levels involved. Under this condition  $K$  is equal to  $3S\lambda/2$ , where  $S$  is the isotropic stress value and  $\lambda$  is the magnetostriction constant ( $-37 \times 10^{-6}$  for polycrystalline nickel). For the film-field geometry mentioned above, the isotropic stress can be expressed in terms of the resonance fields (the field where absorption of microwave power is maximal) as

$$S = (M_s/3\lambda)(H_{R\perp} - H_{R\parallel}). \quad (1)$$

The value of the saturation magnetization  $M_s$  was assumed to be the same as that of bulk Ni, 490 emu/cm<sup>3</sup>, in accordance with conclusions of Neugebauer.<sup>2</sup>  $H_{R\perp}$  is the calculated ideal resonance field for  $S=0$  and was taken as 9200 G in this case ( $\nu=9.3 \times 10^9$  sec<sup>-1</sup>,  $g_{Ni}=2.18$ ). The demagnetizing factor perpendicular to the film was taken equal to  $4\pi$ , which is valid only for a continuous film. Neugebauer<sup>2</sup> showed that films made under the conditions used in this study are indeed continuous. For  $H_{R\perp}$  measured on a reportedly stress-free Ni film, Pomerantz *et al.*<sup>3</sup> gave a value of 9200 G ( $\nu=9.023 \times 10^9$  sec<sup>-1</sup>), which is equal to the value adopted here.  $H_{R\perp}$  is the observed resonance field. For  $H_{R\perp} > 9200$  G,  $S$  is negative (compressive stress); for  $H_{R\perp} < 9200$  G,  $S$  is positive (tensile stress).

The great advantage of this method of stress measurement is that it is applicable to films as thin as 20 Å. Further, it avoids the confusion, encountered in the bending plate method, concerning the sign of the stress in the case of a surface free energy contribution.<sup>4</sup> In the latter method a positive surface free energy

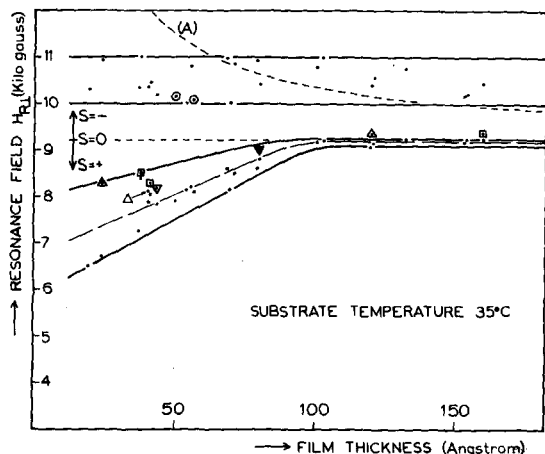


Fig. 1. Upper band: •, Films as prepared in UHV; ○, pure N<sub>2</sub> (100 Torr). Lower band: After adsorption of gases, ◻, pure H<sub>2</sub> (100 Torr); Δ, pure H<sub>2</sub>O (10 Torr); ∇, pure CO (100 Torr); •, pure O<sub>2</sub> (100 Torr); pure N<sub>2</sub>O (100 Torr) or, air (1 atm).

(compressive stress) results in a deflection of the plate indicating tensile stress. The FMR method is however limited to ferromagnetic materials with a large value of  $\lambda$ .

The films as prepared in UHV all show high values of  $H_{R\perp}$ , indicating compressive stress (upper band, Fig. 1), in the range of  $-4$  to  $-8 \times 10^9$  dyn/cm<sup>2</sup>. Hoffman<sup>4</sup> suggests six sources for intrinsic stresses in films, most of them relating to tensile stress. The obvious choice for the compressive stress encountered here is surface free energy. The apparent stress caused by surface free energy can be presented by

$$S = -(\gamma_1 + \gamma_2)/t, \quad (2)$$

where  $\gamma_1$  and  $\gamma_2$  are the surface free energies of the metal at the film/vacuum and film/substrate interface, respectively, and  $t$  is the film thickness. If the substrate is assumed to be indifferent with respect to the film,  $\gamma_2$  becomes equal to  $\gamma_1$ . An approximate value for  $\gamma_1$  at 298°K of 2500 erg/cm<sup>2</sup> was estimated. In Fig. 1 curve (A) represents the  $H_{R\perp}$  values calculated from Eq. (2), substituting  $\gamma_1 = \gamma_2 = 2500$  erg/cm<sup>2</sup> and using Eq. (1) to convert stresses into resonance fields.  $H_{R\perp}$  values of clean films thicker than 60 Å agree acceptably with the calculated values. The fact that these  $H_{R\perp}$  values are mostly higher than predicted and widely scattered may be due to variations in the roughness factor of the films. Equation (2) is valid for a film with roughness factor 1, in practice the roughness factor has a value between 1 and 2. For films thinner than 60 Å, the agreement with Eq. (2) is poor.

Adsorption of gases such as pure H<sub>2</sub>, H<sub>2</sub>O, O<sub>2</sub>, N<sub>2</sub>O, CO, and air appeared to reduce the compressive stresses. The values of  $H_{R\perp}$  in the presence of high pressures of gas are shown in the lower band of Fig. 1. The stress level dropped to below  $\pm 0.3 \times 10^9$  dyne/cm<sup>2</sup> for films thicker than 100 Å. In the adsorption process,  $M_s$  was assumed from Neugebauer's experiments to be unchanged. For films of 100 Å and thinner, the apparent stress changes sign. The reason for this change is now being explored. Several explanations are possible: (a) A change of stress from compressive to tensile (as indicated in Fig. 1) due to the interaction of adsorbed gases with imperfections in the film or due to the surface layer formed by adsorption; (b) no change of sign in stress but the presence of islands instead of a continuous film, leading to a demagnetizing factor less than  $4\pi$ ; (c) an extra (negative) contribution to  $K$  due to film roughness.

Release of stress proceeded at very low pressures; H<sub>2</sub> was active at  $5 \times 10^{-8}$  Torr and other gases were active at slightly higher pressures. Stress release took at least 30 min for H<sub>2</sub> at  $5 \times 10^{-8}$  Torr, for example. This time is longer than the time

required to form a monolayer when the sticking coefficient is between 0.1 and 1, indicating the release of stress is accompanied by diffusion of gas atoms into the film or to the metal/substrate interface. For H<sub>2</sub>, H<sub>2</sub>O, and CO, stress release was not as complete as for O<sub>2</sub>, N<sub>2</sub>O, and air; admission of air resulted in a small additional release of stress. N<sub>2</sub> showed no activity but is reported in the literature not to adsorb on Ni at room temperature.

Neugebauer<sup>1</sup> studied, by torque measurements, the influence of the adsorption of pure H<sub>2</sub> and O<sub>2</sub> on thin Ni films prepared in UHV. From the values of  $K$ , it was concluded that the films as prepared were under tensile stress and that admission of H<sub>2</sub> had no final effect on the value of  $K$ . These two observations are in contradiction to those reported here. To explain the observed changes in the value of  $K$  after admission of O<sub>2</sub>, Neugebauer suggested an increase in tensile stress due to matching between nickel atoms in the nickel oxide and the underlying nickel film. On the basis of the work presented here, it is obvious that superimposed on the tensile stress in a clean film is the compressive stress due to surface free energy. Admission of O<sub>2</sub> releases the compressive component of the stress, resulting in an apparent increase in tensile stress. It remains to be explained why Neugebauer invariably found tensile stress in Ni thin films, these films being apparently equivalent to those investigated in this study.

\* This research was supported by the Advanced Research Project<sup>8</sup> Agency, Department of Defense, through the Office of Naval Research under Contract No. Nonr 610(09).

† On leave from Laboratory for Physical Chemistry, Technological University, Eindhoven, Netherlands.

<sup>1</sup> C. A. Neugebauer, Trans. Vacuum Symp. 8th 1961, 924 (1962).

<sup>2</sup> C. A. Neugebauer, Phys. Rev. **116**, 1441 (1959).

<sup>3</sup> M. Pomerantz, J. F. Freedman and J. C. Suits, J. Appl. Phys. **33**, 1164 (1962).

<sup>4</sup> R. W. Hoffman, *Physics of Thin Films* (Academic Press Inc., New York, 1966), Vol. 3, p. 211 ff.

## Thermal Expansion Coefficients of Ruby Muscovite Mica\*

LESTER GOLDSTEIN AND BEN POST

Physics Department, Polytechnic Institute of Brooklyn,  
Brooklyn, New York 11201

(Received 23 December 1968; in final form 29 January 1969)

In connection with efforts to grow thin single crystals of noble metals by vapor deposition on mica substrates, we have been concerned with the degree of anisotropy of the thermal expansion of mica and with the effects of such expansion on the quality and properties of the metal crystal. Our work has been concerned with specimens of ruby muscovite mica purchased from Asheville-Schoonmaker Mica Company, Newport News, Virginia. Mica crystallizes in the monoclinic system. It cleaves easily into thin sheets perpendicular to the  $c$  axis. The lattice constants of the specimens with which we worked were  $a = 5.184$  Å,  $b = 9.043$  Å, and  $c = 19.92$  Å, which agree well with corresponding values in the literature. For example, Donnay<sup>1</sup> quotes values of  $a = 5.19$  Å,  $b = 9.03$  Å, and  $c = 20.05$  Å. Our measurements of the  $\beta$  angle did not reveal any significant difference from the value of  $\beta = 95^\circ 46'$  quoted by Donnay. Our primary interest in this investigation was in the relative expansions of the  $a$  and  $b$  axes and the possible changes in the  $\beta$  angle with temperature.

There are very few data concerning the relative thermal expansions of the  $a$  and  $b$  axes in the literature. Much of the available data on the thermal expansion of mica has been collected in a table prepared by the National Bureau of Standards in 1945.<sup>2</sup> Most of the measurements reported there were carried out by dilatometry and strain-gage techniques. Although several reasonably consistent values for  $\Delta c/c$  are listed, data of the type in which we were interested are not included. In general, only