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RESEARCH ON SURFACE PROPERTIES OF Ni FILM AND NiSe-COATED Ni FILM

(Part 2)

By

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The effect of hydrogen and ammonia adsorption on the work function of an evaporated Ni film or a NiSe-coated^{**)} Ni film was investigated by the vibrating condenser method, the contact potential difference (c. p. d.) between these films and a vibrating reference electrode of Au being measured in atmospheres of hydrogen, ammonia and hydrogen-ammonia mixture. Adsorption of hydrogen on Ni film was found to increase the work function and to decrease its electric resistance. In the presence of hydrogen-ammonia mixture work function of the NiSe-coated Ni film increased monotonously with temperature over the range from 20°C to 80°C. Illumination changed c. p. d. of a NiSe-coated Ni film in the presence of ammonia whereas not at all in its absence; the result indicated that adsorbed ammonia was positively charged.

Introduction

The present authors studied in Part 1¹⁾ the effects of hydrogen or ammonia adsorption on the work function of evaporated Ni film or NiSe-coated^{**)} Ni film by means of the retarding potential method. The method proved, however, rather unsatisfactory, since the thermionic emission measurement requires high vacuum around the electron emitter. The vibrating condenser method²⁾ was used instead for the present measurement of c. p. d. between the above-mentioned films and a vibrating reference electrode of Au in atmosphere of hydrogen, ammonia and hydrogen-ammonia mixture. The electric resistance (ρ) of the Se films was determined for investigating their state. The surface photo-effect of a NiSe-coated Ni film in ammonia atmosphere

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^{**)} The surface is completely coated with crystallite of β -NiSe, as concluded from the results of X-ray diffraction, electron diffraction and electron microscopy. T. MATUI and K. AZUMA, *Shokubai Catalyst* No. 10, 14 (1954) (in Japanese).

1) K. AZUMA and A. KOBAYASHI, *This Journal* 4, 152 (1956).

2) H. PALEVSKY, R. K. SWANK and R. GRECHIK, *Rev. Sci. Instr.* 18, 298 (1947); I. NAKATA and I. OGAWA, *Seisan Kenkyu* 5, 59 (1953) (in Japanese).

was further observed by BRATTAIN and BARDEEN's method³⁾ used for the study of the space charge layer near the surface of germanium, for the information on the sign of the charge of adsorbed ammonia on the film.

I. Apparatus and Procedure

A. Cells for contact potential, electric resistance and surface photo-effect measurements.

Both the cells C(I) (sliding electrode type) and C(II) (rotating electrode type) of hard glass were used for the measurement of the contact potential and the latter alone for the resistance and the surface photo-effect measurements.

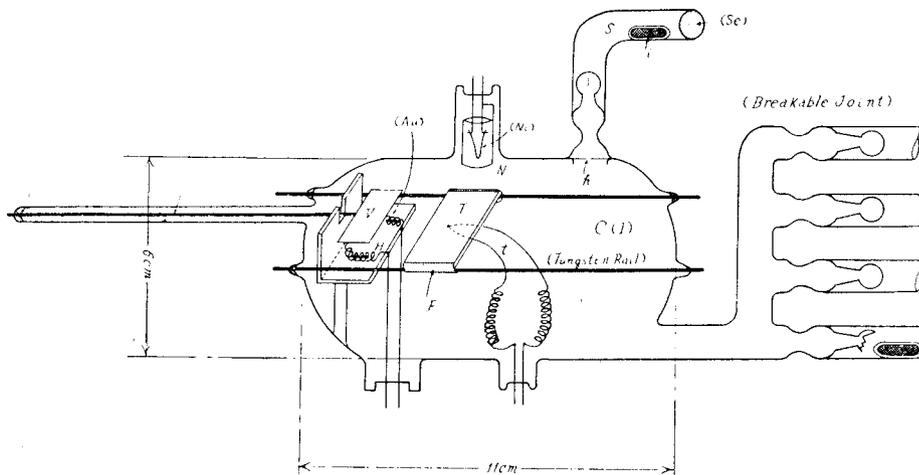


Fig. 1 a Sliding electrode type cell, C-I.

The cell C(I) is shown in Fig. 1 a. A glass plate of $2.5 \times 1.5 \text{ cm}^2$ area is mounted on a pair of guiding rods of tungsten by means of Fernico metal hooks welded to both sides of the plate so as to slide the latter along the guiding rods by tilting the cell. The test electrode T is prepared by depositing Ni on the upper surface of the glass plate at 60°C in vacuo evaporated from nickel filament (Ni) in a guard cylinder N of thin Ni plate; the hooks and guiding rods serve as leads. V is the vibrating reference electrode of nickel plate of $2 \times 1 \text{ cm}^2$ area, on which Au film is deposited by evaporating Au wire held in a

3 W. H. BRATTAIN, *Semi-conducting Materials*, p. 37 1951; W. H. BRATTAIN and J. BARDEEN, *Bell. System Tech. Jour.* 32, 1 1953.

tungsten coil H, which is the heater of the test electrode as well. V is welded to a tungsten rod w of 1 mm diameter and 10 cm length fixed in a glass tube v of 5 mm diameter. The temperature of the test electrode is measured by a tungsten-nickel thermocouple t with its welded junction embedded into T from its lower surface.

Fig. 1 b shows the cell C (II). The test electrode T is a glass casket of $2.5 \times 1.5 \text{ cm}^2$ upper surface, on which Ni film is deposited by evaporating filament (Ni) in a guard cylinder N of nickel at the same condition as in the case of C (I). The casket is pivoted on a glass joint

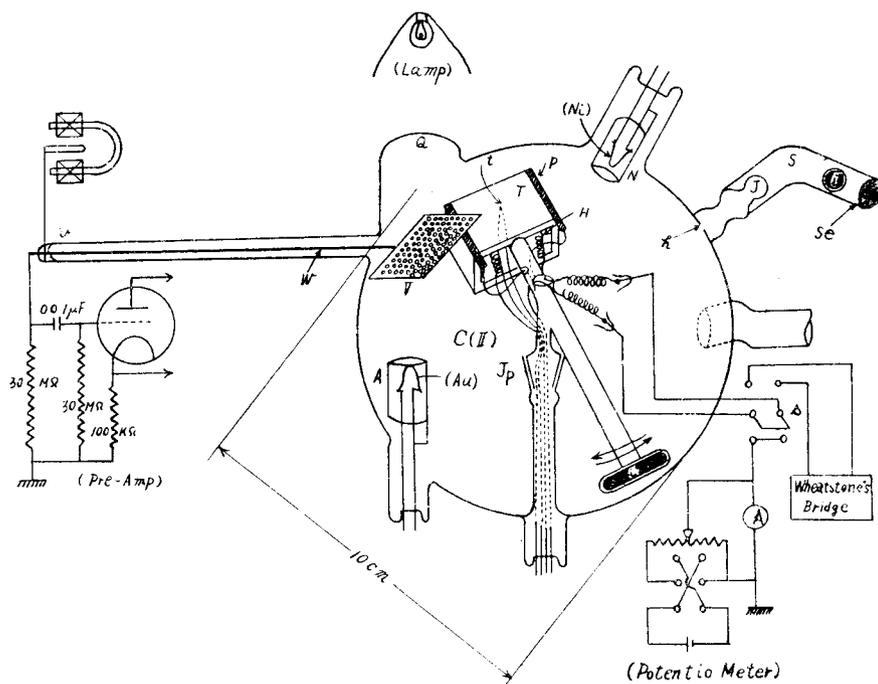


Fig. 1 b Rotating electrode type cell, C (II)

J_1 , and turned around by means of a piece of iron i sealed inside and a magnet outside. T is heated by a tungsten coil heater H inside the casket, the surface temperature being measured by a tungsten-nickel thermocouple t, embedded into the glass plate from the surface opposite to that of Ni deposition. Two platinum strips P are welded on the edges of the upper surface of T and led outside by means of nickel ribbons as shown in Fig. 1 b. The vibrating reference electrode V is a gold-plated nickel net of $2 \times 1 \text{ cm}^2$ gross area mounted in the cell

similarly as in the case of C(I). The net of V allows the light of an incandescent lamp led inside from the quartz window Q to pass through to illuminate the NiSe-coated Ni film of T.

B. Materials.

Ni: spectroscopically pure grade Ni filament of 0.25 mm diameter was used for (Ni) of C(I) and C(II).

Au: analytically pure grade Au wire of 0.5 mm diameter was used for the evaporated Au film on V.

Se: analytically pure grade selenium powder (Kahlbaum) was thoroughly degassed and sealed in a glass tube S shown in Figs. 1a and 1b. Its vapour was allowed to effuse through a pin-hole h in a thin platinum plate welded to the glass wall; the vapour was deposited on the Ni film of T, which was then brought right beneath h as described in Part 1.¹⁾

H₂: hydrogen was electrolytically prepared, passed through an electrically heated palladium thimble and stored in a flask.

NH₃: cylinder ammonia was passed over caustic potash and soda lime, fractionated several times by distillation and stored in a flask.

C. Experimental method.

Measurements of the contact potential in the presence of gas were carried out as follows. The cell was thoroughly degassed by evacuating

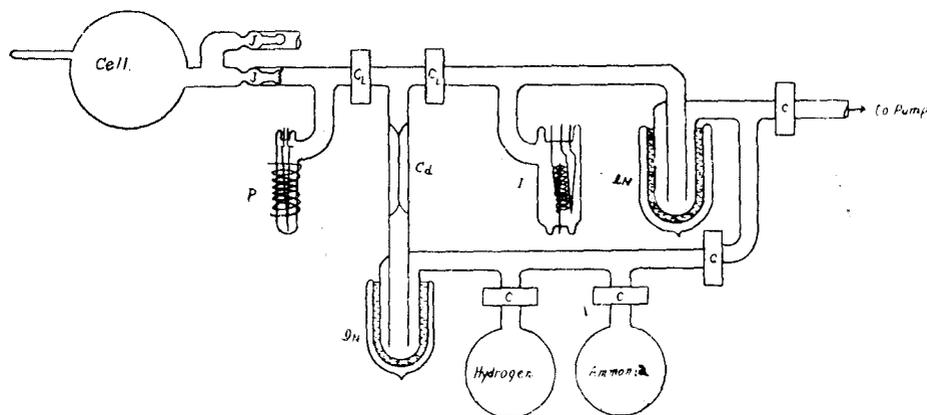


Fig. 1 c Schematic sketch of apparatus

- | | |
|---------------------------------------------------|------------------------|
| J: Breakable Joint | Ca: Capillary Leak |
| P: Pirani Gauge (Dardel Type) | LN: Liq. Nitrogen Trap |
| I: Ionization Gauge (Bayard-Alpert Type) | c: Vacuum Tap |
| c ₁ : Greaseless Cone-and-Socket Joint | |

it to $ca. 10^{-7}$ mmHg pressure, in an electric furnace at 450–500°C for several days. Sample gas was introduced into the cell from one gas reservoir through a capillary leak C_d shown in Fig. 1c, and the cell was cut off from the vacuum line at a breakable joint J or a greaseless joint c_L . The pressure of gas in the cell was measured by a pirani gauge P of a constant temperature type.⁴⁾

The test electrode T was faced with the vibrating reference electrode V about 1 mm apart from each other and the latter was driven electromagnetically at its resonant frequency 370 cps through $ca. 0.1$ mm amplitude. Vibration of V varied the capacity sinusoidally giving rise, if there existed any potential difference between surfaces of V and T, to an electrical signal, which was transmitted to pre-amplifier connected with V. The signal was reduced to zero by applying the d. c. potential across the potentiometer connected between V and T. The d. c. potential is equal and opposite to c.p.d., provided

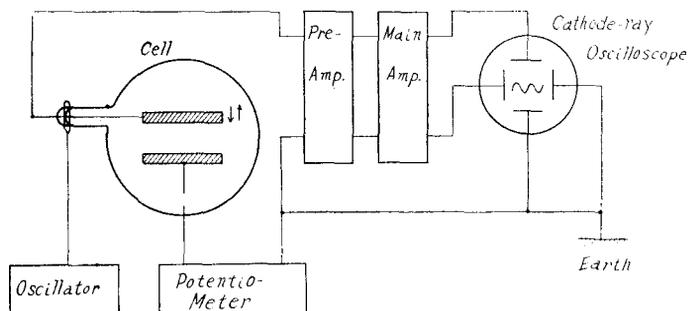


Fig. 2 Block diagram of circuit.

that the subsidiary effects of vibration are absent. The vanish of the signal was detected by means of a selective amplifier of gain 100 db with an oscilloscope at the final stage of the amplifier. The block diagram of the circuit is shown in Fig. 2. The cell was kept in a shielded box to avoid disturbances of stray fields, temperature and light. Relative accuracy was 2–5 mV or 5–10 mV in the case respectively of high vacuum or of gaseous atmosphere.

The electric resistance ρ of the films in C(II) was measured by means of a Wheatstone bridge. The measurements of ρ and c.p.d. were carried out alternatively by turning over a switch s shown in Fig. 1b.

4) G. DARDEI, J. Sci. Instr. 30, 4 (1953).

TABLE 1. c.p.d. Observation with the cell C(I)

No. of experiments	Date	Surface condition	Temperature of the surface °C	c. p. d. volts	Remarks
1	Dec. 2, 1954	Ni	17	+ 0.82 ₆	1000 Å thickness; 5 hrs. after evaporation.
	Dec. 3, "	Ni	20	+ 0.88 ₉	35 hrs. after the above measurement.
2	Dec. 3, "	Ni+H ₂ (4×10 ⁻¹ mmHg)	17	+ 0.83 ₅	
3	Dec. 3, "	Ni+H ₂ (4×10 ⁻¹ mmHg) +NH ₃ (21 mmHg)	17	+ 0.19 ₀	
4	Dec. 7, "	NiSe	22	+ 0.04 ₇	100 molecular layers of Se ₈ molecules on Ni and heat-treatment for 12 hrs. at 180°C.
5	Dec. 9, "	NiSe+H ₂ (5×10 ⁻¹ mmHg)	17	+ 0.05 ₂	
6	Dec. 10, "	NiSe	17	- 0.00 ₉	Evacuation for 1 hour at 200°C.
7	Dec. 10, "	NiSe+NH ₃ (42mmHg)	19	+ 0.05 ₄	

TABLE 2. c.p.d. Observation with the cell C(II)

No. of experiments	Date	Surface condition	Temperature of the surface °C	c. p. d. volts	Remarks
1	Feb. 26, 1955	Ni	17	+ 0.27 ₆	Film of 100 Å thickness; 20 hrs. after evaporation.
2	Feb. 26, "	Ni+H ₂ (1 mmHg)	17	+ 0.24 ₆	
3	Feb. 26, "	Ni+H ₂ (1 mmHg) +NH ₃ (31 mmHg)	17	+ 0.31 ₉	
4	Mar. 15, "	NiSe	19	- 0.02 ₁	Ni film was coated with Se (500 molecular layers of Se ₈ molecules) and above the Se coating Ni was deposited about 30 Å thick. Heat-treatment for 30 hrs. at 200 ~ 250°C.
5	Mar. 16, "	NiSe+H ₂ (3.7 mmHg)	17	- 0.05 ₃	
6	Mar. 16, "	NiSe+H ₂ (3.7 mmHg) +NH ₃ (37.7 mmHg)	16	+ 0.15 ₈	
7	Mar. 20, "	NiSe	21	+ 0.06 ₃	Evacuation for 40 hrs at 250°C.
8	Mar. 20, "	NiSe+NH ₃ (18.5mmHg)	17	+ 0.19 ₆	
9	Mar. 21, "	NiSe+NH ₃ (18.5mmHg) +H ₂ (2 mmHg)	20	+ 0.16 ₁	

II. Results and Discussion

Results are shown in Tables 1~3 and in Figs. 3~9. Each of Tables 1 and 2 shows the result of a series of c.p.d. measurements carried out in succession with C(I) or C(II).

The c.p.d. of Ni film in the cell C(II) in vacuo drifted by about one volt for twenty hours after evaporation as shown in Fig. 3. This effect appears to be due to the recrystallization of Ni deposit.

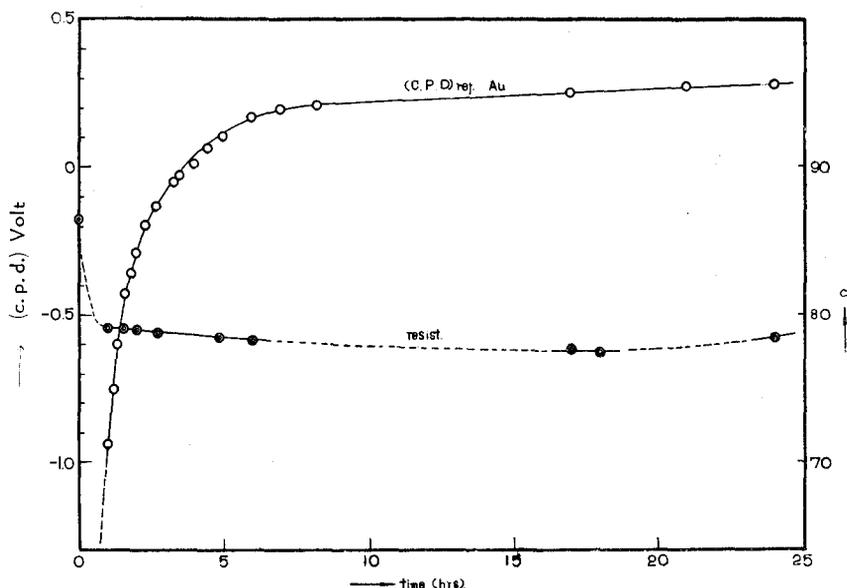


Fig. 3

Drifts of c.p.d. and electric resistance:

○, c.p.d.; ●, ρ.

The c.p.d. between the NiSe and reference electrodes apparently increased by 0.05~0.14 volt, when ammonia was introduced at room temperature as shown in Tables 1 and 2. This increase could hardly be attributed to the change of NiSe work function of T alone, since ammonia might be adsorbed on V as well to change its work function. Fig. 4 shows the variation of the apparent c.p.d. of Ni and NiSe films with temperature in the presence of hydrogen-ammonia mixture observed by changing the temperature of the test electrode surface alone. The partial pressures of hydrogen and ammonia were about 3 mmHg and 30 mmHg respectively. It may be concluded from the

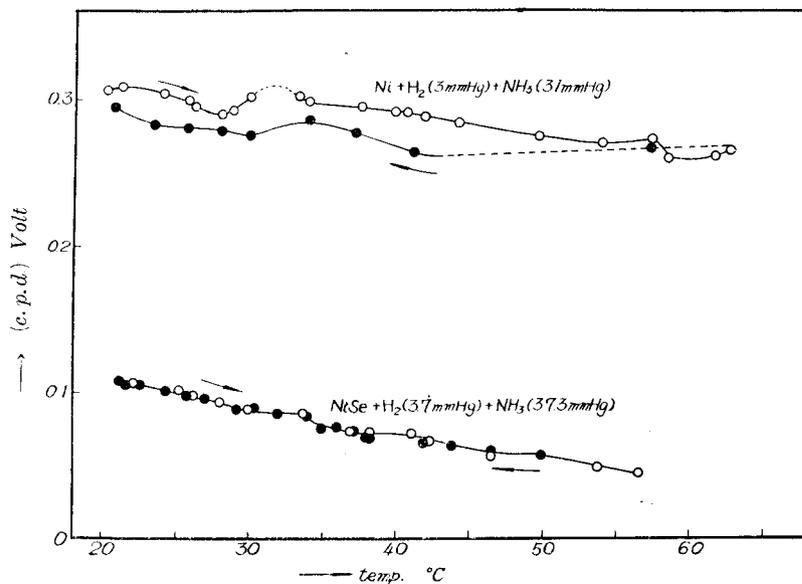


Fig. 4

The c. p. d. between Ni or NiSe films and Au electrode in hydrogen and ammonia mixture; ○ or ●, measured by raising or lowering temperature.

result, inasmuch as the temperature of reference electrode and partial pressures around it may be taken kept practically constant, that there exists no anomalous change of work function of the NiSe film in the temperature range 20~50°C, which might be expected from the experiment of KANEKO and ENOMOTO,⁵⁾ who found an acute N-form change of the exchange rate between hydrogen and heavy ammonia with temperature in the presence of NiSe-coated Ni powder.

The sign of the charge of adsorbed ammonia was determined as below according to BRATTIN and BARDEEN's method.⁶⁾ No increment (Δcp)_L of c. p. d. was observed by the illumination of NiSe-coated Ni film in the absence of NH₃. It is concluded from the result that there exists no barrier layer due to space charge near the surface. In the presence of ammonia c. p. d. was found rapidly and considerably to decrease by illumination but gradually to restore, on putting out the illumination, toward the initial value, as shown in Fig. 5 and Table 3.

5) Y. KANEKO and S. ENOMOTO, Shokubai (Catalyst) No. 6, pp. 8 and 36 (1950); No. 7, p. 98 (1951) (in Japanese).

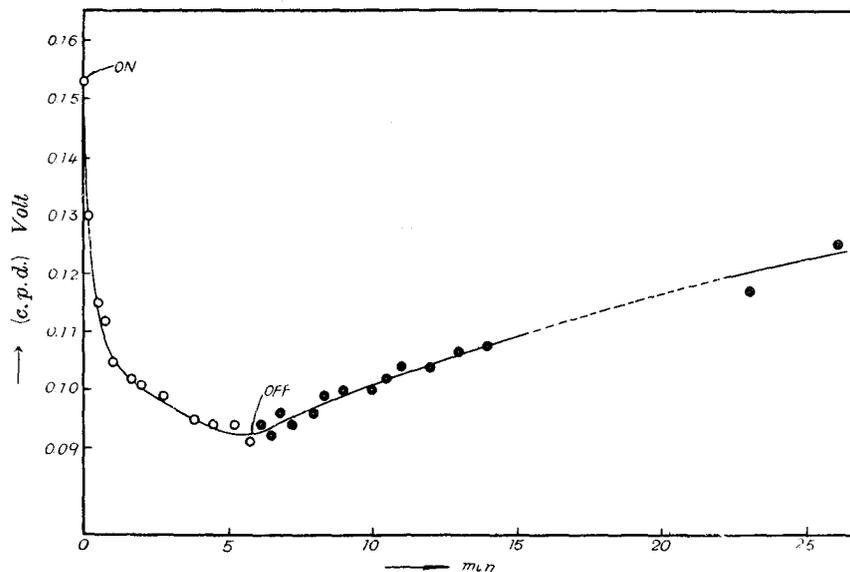


Fig. 5

Change of c.p.d. caused by illumination :
 ○, illuminated; ●, illumination put out.

TABLE 3. Effects of Illumination on NiSe film

Surface condition	$(\Delta cp)_L$ volts	
	at 22°C	at 40°C
NiSe	none	none
NiSe + H ₂	none	none
NiSe + NH ₃	- 0.05 ₂	- 0.10 ₆
NiSe + H ₂ + NH ₃	- 0.05 ₄	- 0.07 ₇

These results show, aside from the effect of ammonia dipoles, that ammonia molecules adsorbed on NiSe film are positively charged to give rise to a negative space charge layer near the surface.

The observed increase of the work function with increasing temperature shown in Fig. 4 is now explained on the ground of the above conclusion that ammonia molecules on NiSe surface are positively charged and of the fact that the amount of ammonia adsorption decreases with increasing temperature. The present result of c.p.d.

decreasing with increasing temperature disagrees with those in Part 1⁶⁾ and of another preliminary report⁶⁾ of the present authors. However, the present result must be reliable, since the measurements of Part 1 were carried out at irreversible condition in high vacuum, and those of the other⁶⁾ by keeping the reference and the test electrodes at the same temperature.

Fig. 6 shows the absence of the variation of c.p.d. of NiSe film with temperature in the presence of hydrogen.

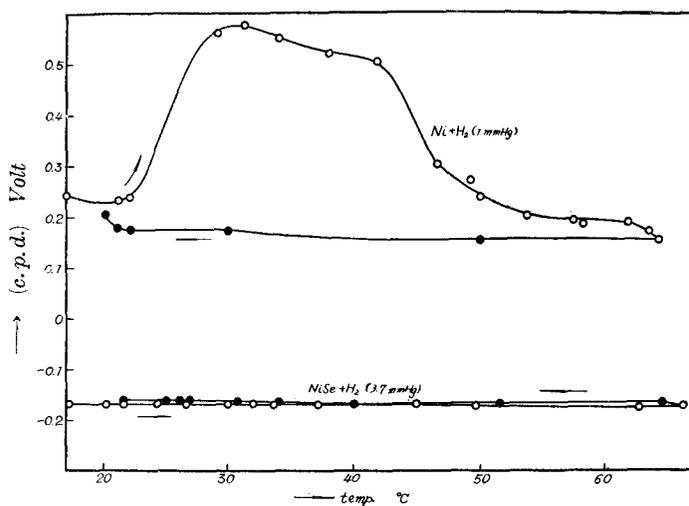


Fig. 6

The c. p. d. between Ni or NiSe films and Au electrode in hydrogen atmosphere; ○ or ●, measured by raising or lowering temperature respectively.

The variation of electric conductivity $1/\rho$ of the NiSe film with temperature was found characteristic of semiconductors, as shown in Fig. 7, the activation energies of $1/\rho$ being 0.8 eV or 0.035 eV respectively at above or below 150°C as observed with the cell C (II).

Hydrogen was found to cause *ca.* 0.03~0.05 eV increment of work function of an evaporated Ni film at room temperature as shown in Tables 1 and 2, admitted that hydrogen does not affect the work function of Au film, qualitatively in accordance with the previous measurement⁷⁾ and the results of other investigators.⁷⁾ Hydrogen de-

6) A. KOBAYASHI and K. AZUMA, *Shokubai (Catalyst)* No. 10, p. 11 (1954) (in Japanese).

7) J. C. P. MIGNOLET, *Discussion of the Faraday Soc.* No. 8, 105 (1950); M. M. BAKER, G. I. JENKINS and E. K. RIDEAL, *Trans. Faraday Soc.* **51**, 1592 (1955).

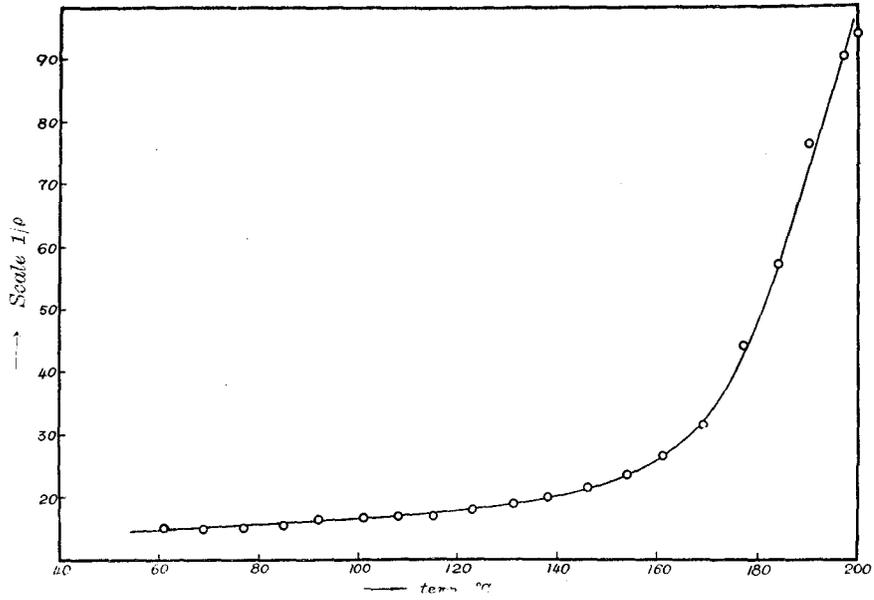


Fig. 7

Relation of $1/\rho$ to temperature.

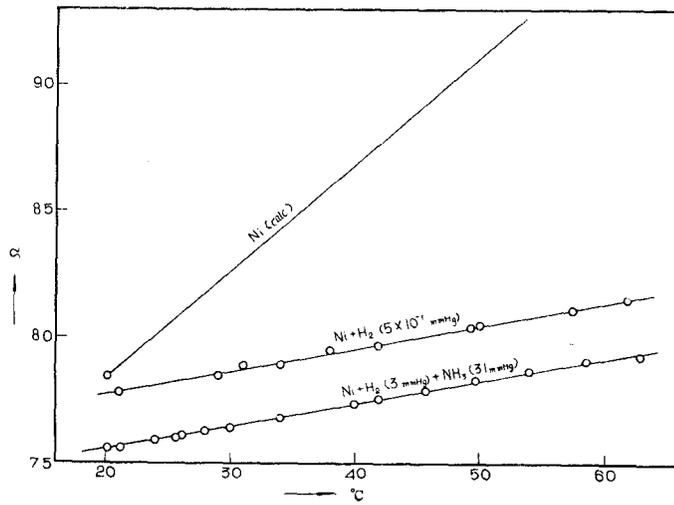


Fig. 8

Electric resistance *versus* temperature of Ni film with ambient gases. Ni (calc.): Calculated from an observation at 20°C and the known temperature coefficient of the resistance of nickel mass.

presses on the other hand electric resistance ρ by about 0.8% at 20°C as shown in Fig. 8; this result contradicts with that of SUHRMANN and SCHULZ on their "fresh" Ni films^{8), ***)}. An appreciable fluctuation has, however, been observed in the present measurement of c.p.d. and ρ with the cell C(II) at room temperature over the pressure range from 10^{-2} to 10^{-1} mmHg of hydrogen as shown in Fig. 9. Further investigations of the nickel-hydrogen system in higher vacuum are now in

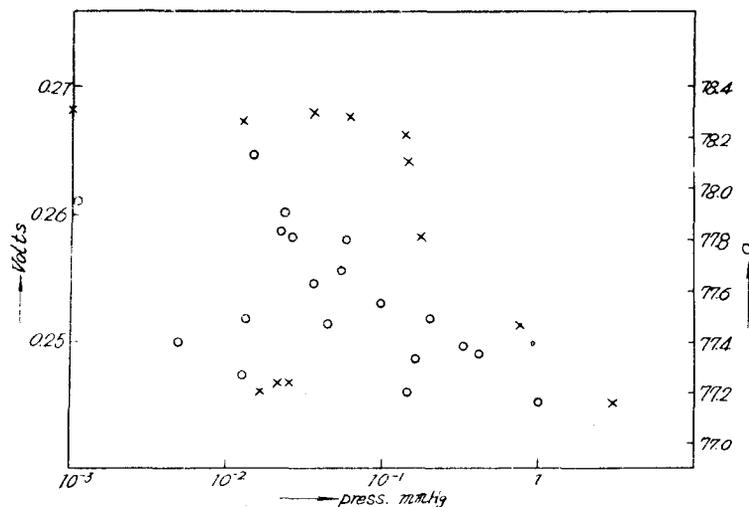


Fig. 9

The c.p.d. (O) and ρ (X) at room temperature in atmosphere of hydrogen.

progress in this laboratory.

The authors are much indebted to Prof. J. HORIUTI, the Director of this Institute for suggesting this problem. They also wish to express their cordial thanks to Messers. T. NAKAMURA and T. TAKAISHI for stimulating discussions; and to Messers. T. NAKADA and K. SEINO for their earnest help in glass-blowing.

***) Mr. Z. ODA (The Electrical Communication Laboratory, Nippon Telegraph and Telephone Public Cooperation, Tokyo) has recently communicated us privately that he found the effect of a small amount of oxygen of the electric resistance of Ni evaporated film in hydrogen preliminarily evacuated to $<10^{-7}$ mmHg, pointing out a possible contamination of the evaporated Ni film in our case when the cell was preliminarily evacuated to 10^{-7} mmHg.

8) W. M. H. SACHTLER, J. Chem. Phys. 25, 751 (1956).

R. SUHRMANN and K. SCHULZ, Naturwis. 42, 340 (1955); Z. f. phys. Chem. 1, 69 (1954).