# 725. *The Surface Chemistry of Germanium. Part I. Chemical Effects at* pn *Junctions.*

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Deviations in the current–voltage characteristics of reverse-biassed germanium *pn* junction diodes exposed to various environments are summarised. Further observations are reported which suggest a mechanism correlating the electrical effects of the gas on the diode with its chemical properties. The electron affinity (or ionisation potential) of the adsorbate and the work function of the germanium are related to the equilibrium conditions occurring at the surface.

Highly purified germanium at room temperature has been shown to contain equal numbers of conducting electrons and positive holes, which implies that the net concentration of residual donor or acceptor impurities is too small to move the Fermi level from its position mid-way between the bottom of the conduction band and the top of the valency band. By suitable addition of donor (Group V) or acceptor (Group III) impurities an excess of conducting electrons or holes may be introduced. The material is then said to be of the *n*-type or *p*-type respectively. When a transition from *n*- to *p*-type conduction occurs in an otherwise homogeneous germanium sample the resulting *pn* junction behaves as a rectifier of electric current. This device has been described by Shockley,[1] whose analysis yields the following expression for the dependence on applied voltage of the current flowing across the junction :

Fig. 1. *Theoretical characteristic of a* pn *junction.*

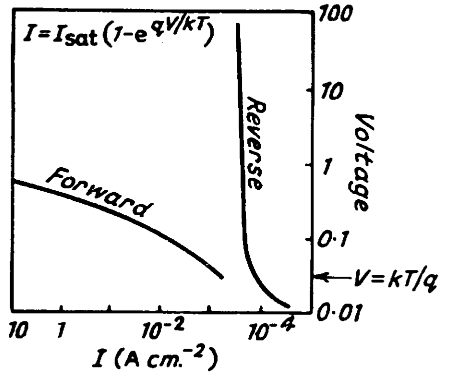
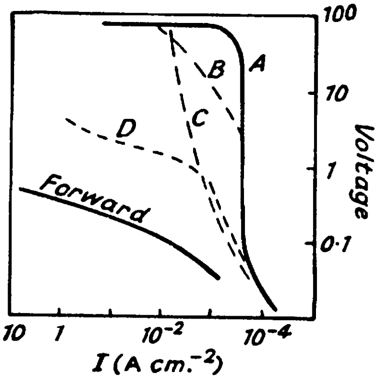


Fig. 2. *Characteristics exhibited by real diodes.*



$$I = I_{\text{sat}}[1 - \exp(qV/kT)] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $I$ is the current flowing for a bias $V$ at temperature $T$. The constant $I_{\text{sat}}$ is determined by the equilibrium concentrations and lifetimes of minority carriers in the material on both sides of the junction. $I_{\text{sat}}$ is very temperature-dependent, but is voltage-independent up to a few tens of volts if the material on at least one side of the junction has a resistivity of 1 ohm cm. or more. It can be seen that the current will saturate at the value $I_{\text{sat}}$ for a negative applied bias of a few times $kT/q$, while it will increase indefinitely for a positive applied bias (Fig. 1). Clearly this device is an efficient rectifier.

Germanium *pn* junctions have been made by a variety of methods and found to exhibit current–voltage characteristics in excellent agreement with eqn. (1) up to a voltage at which breakdown phenomena, not considered in the derivation of the equation, set in, provided

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[1] Shockley, *Bell Syst. Tech. J.*, 1949, **28**, 435.

their surface is suitably treated after manufacture and suitably protected against subsequent contamination (Fig. 2, curve *A*). Unsuitable surface treatment leads to the types of deviation shown in curves *B*, *C*, and *D* of Fig. 2: From a study of these deviations conclusions can be drawn concerning the mechanism of chemisorption at semiconductor surfaces. It will be shown that anomalous *pn* junction characteristics arise by a mechanism akin to that occurring in heterogeneous catalysis, as described by Dowden.[2]

Deviations of type *B* have been ascribed to the presence of a surface film of water [3] which causes a leakage current approximately proportional to the applied voltage. Law [3] explains this effect in terms of electrolytic surface conduction: he has shown that the excess of reverse current begins to increase appreciably only when the relative humidity reaches the value at which the adsorbed water becomes mobile and that the measured conductance is in good agreement with the value expected from a mass-spectrographic estimation of the surface density of adventitious ions. A number of investigators have however been unable to find any evidence for the mass transfer which should result from such a mechanism, and McWhorter [4] concludes that the current is carried by a non-electrolytic process, possibly by electrons jumping from one trap to another in a direction parallel to the surface.

FIG. 3. *Energy-band diagram for an* n-*type semiconductor with positive surface-space charge.*

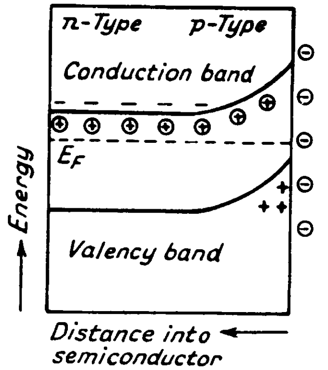
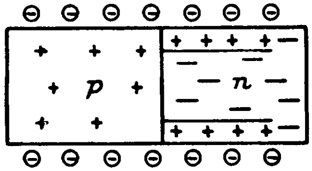


FIG. 4. *Effect of channel formation on rectifying area.*



Deviations of type *C* are explained by extending the concept of surface states and space-charge regions which are postulated at the free surface of a semiconductor.[5, 6] A model has been developed for the state of affairs at the surface of a *pn* junction covered by an ionic layer. Fig. 3, representing the energy diagram of *n*-type material covered with a layer of negative ions, shows that the presence of such a layer results in the build-up of a positive space-charge near the semiconductor surface, this space-charge consisting predominantly, for small surface densities of ions, of ionised donor centres (not neutralised by mobile electrons). As the surface density of negative ions increases, the concentration of mobile holes near the surface eventually predominates, giving rise to a surface inversion layer which behaves as *p*-type material and is called a "channel." [7] Fig. 4 depicts the increase in the effective rectifying area of a *pn* junction diode resulting from the formation of such a channel. The extra rectifying area has been shown [8] to depend on the applied bias in a way consistent with the commonly observed deviations of the type shown in Fig. 2, curve *C*. A similar argument applies to *n*-type channels on the *p* side. Although

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[2] Dowden, *J.*, 1950, 242.

[3] Law, *Proc. Inst. Radio Engineers*, 1954, **42**, 1367.

[4] McWhorter, Massachusetts Inst. Technol., Lincoln Lab. Tech. Report No. 80, May 20, 1955, p. 51.

[5] Bardeen, *Phys. Rev.*, 1947, **71**, 717; Shockley and Pearson, *ibid.*, 1948, **74**, 232; Bardeen and Brattain, *Bell Syst. Tech. J.*, 1953, **32**, 1.

[6] Garrett and Brattain, *Phys. Rev.*, 1955, **99**, 2, 376.

[7] Brown, *ibid.*, 1953, **91**, 518.

[9] Christensen, *ibid.*, p. 1371.

[8] McWhorter and Kingston, *Proc. Inst. Radio Engineers*, 1954, **42**, 1376.

the existence of a channel can be demonstrated unequivocally only by a photoinjection method, as used by Christensen[9] and McWhorter and Kingston,[8] it seems fairly certain that a curve of type *C* must indicate channel formation. No alternative mechanism has been put forward which could account for the shape of this curve, neither have instances been reported of type-*C* curves not caused by channels. Further evidence in support of the assumption made here that atmospheres which cause the reverse characteristic to assume shape *C* do so by inducing channels is provided by experiments on alloy-junction transistors carried out by Mr. F. F. Roberts, of this Station, who found that changes in atmosphere giving rise to type-*C* characteristics also increased the capacitance of the collector and the current gain of the device, demonstrating that the atmosphere under test had caused an increase in the collector area, and therefore a channel.

When surface electrical breakdown phenomena occur in addition to the above mentioned effects curves of type *D* are obtained.

So far only oxygen has been shown [7,8,9] to cause *p*-type channels on the *n* side, and water the opposite type of channel under certain conditions.

In this paper the effect of other oxidising agents, such as nitrogen peroxide and the halogens, is considered, and the behaviour of the diode in the vapours of the ionising solvents ammonia, sulphur dioxide, and water is described. Expressions are also obtained for the equilibria between adsorbate and surface in terms of the electron affinity (or ionisation potential) of the former and work function of the latter.

## EXPERIMENTAL

All experiments were carried out on a set of four junction diodes prepared by alloying indium at 500° on 3 ohm cm. *n*-type germanium in a hydrogen atmosphere. The diodes were degreased with trichloroethylene and etched electrolytically in a solution containing 5·5 g. of sodium hydroxide and 4·0 g. of disodium dihydrogen ethylenediaminetetra-acetate in 100 ml. of distilled water. A current of 5 mA was passed for about 1 min., the diode being the anode and a platinum electrode the cathode. After being rinsed with de-ionised water the diodes were mounted in a borosilicate-glass manifold (Fig. 5).

Atmospheres of pure nitric oxide, nitrogen peroxide, iodine, bromine, water, sulphur dioxide, and ammonia were individually introduced into the manifold.

*Nitric Oxide.*—The crude gas was generated from nitric acid (*d* 1·20) and copper and collected in cold saturated aqueous ferrous sulphate. Flask *R* containing the $FeSO_4,NO$ complex was joined to the purifying system (Fig. 6). Nitrogen was blown through the whole system, including the manifold, to displace most of the air present. Tap *G* was then closed and the system was evacuated to about 30 μm. Tap *H* was closed and *G* opened so that nitrogen again filled the apparatus. Evacuation was repeated, and finally water was drawn up into *M* by closing *K* and *L* and manipulating *G*. The system was evacuated to 10 μm. and taps *E*, *D*, and *H* were closed. The characteristics of each diode could then be measured in a vacuum. Tap *L* was next opened and the $FeSO_4,NO$ solution slowly warmed so that nitric oxide collected in reservoir *M*. When sufficient nitric oxide had been generated, *L* was shut and the gas slowly admitted into *I* by opening *G* and *F*, the pressure being noted on the manometer *J*. Flask *I* contained nitric oxide, a trace of nitrogen, and some moisture. Nitrogen has been shown to have no effect on germanium *pn* junctions;[10] the water was frozen out by the trap *O* at −80°. Known amounts of pure nitric oxide could thus be introduced into the manifold *via* the taps *E* and *D*, which were used as a gas pipette.

*Nitrogen Peroxide.*—Lead nitrate was heated electrically in a slow stream of oxygen and the gases were passed over lead peroxide and phosphoric oxide into a trap at −20°. From this, nitrogen peroxide was sublimed under reduced pressure into a trap at −80°. This was connected to the manifold at *D* and used as a source of nitrogen peroxide. The pressure of nitrogen peroxide in the system was controlled by the use of suitable cooling agents, after the system had been evacuated with the cold trap at −180°, and sealed off at *B*.

*Bromine.*—Owing to the absorption of bromine by tap-grease it was necessary to work in a tap-free apparatus. The system was sealed off at the constriction *A* (Fig. 5) and outgassed by prolonged pumping. The vacuum was released and the end *P* opened. Some drops of bromine

[10] Law and François, *Ann. N.Y. Acad. Sci.*, **1954**, **58**, 925.

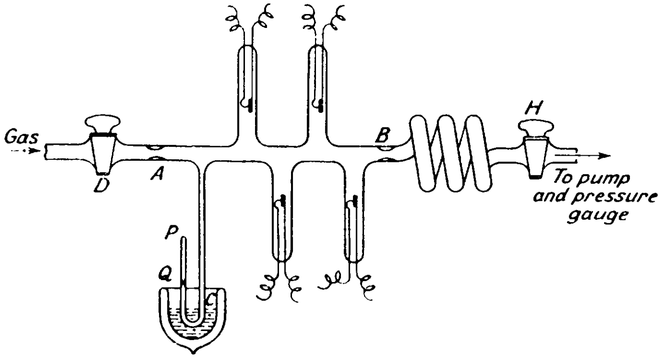
were introduced into the tube *C*, which was surrounded by liquid air, and the tube was quickly sealed at the constriction *Q*. The system was evacuated with the liquid-air trap in position and sealed off at the constriction *B*. The vapour pressure of bromine in the diode enclosure could be controlled by suitable choice of the freezing agent around *C*.

*Iodine*.—A technique similar to that for bromine was used.

*Water*.—A small flask of distilled water was sealed on to the manifold, and the pressure of water vapour allowed into the evacuated system was controlled by a gas-pipette and measured on an oil-manometer.

*Sulphur Dioxide*.—After the system had been outgassed by prolonged pumping, commercial sulphur dioxide (A. Boake Roberts and Co.) was admitted to 1 atm. pressure and the system was closed. The concentration of sulphur dioxide could be varied by placing limb *C* in cooling baths of various temperatures.

FIG. 5. *Manifold and cold finger.*



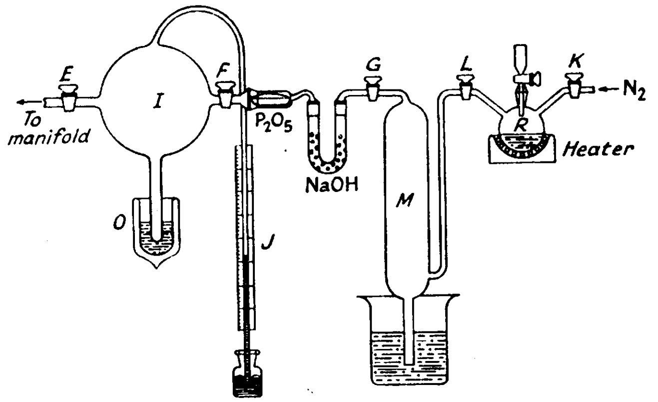


FIG. 6. *Purification of nitric oxide.*

*Ammonia*.—Pure dry ammonia, obtained from a gas cylinder (Anhydrous Ammonia Co.), was introduced into the system. The concentration was again controlled by freezing.

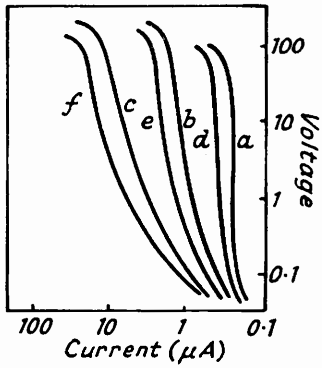
## Results

The diodes were exposed to each ambient gas in turn, over a range of pressures, and their characteristics were observed, d.c. from a high-impedance source being used. Some time effects were observed in the experiments with ionising solvents, especially in the region of the characteristic where the power dissipated was sufficient to " boil off " the adsorbed layers, but not in the experiments with oxidising atmospheres. With nitrogen peroxide, bromine, and iodine it was expedient to pump or freeze off the excess of gas to avoid excessive attack on the device. This was thought permissible because equilibrium chemisorption was almost instantaneous and practically irreversible for any particular gas-pressure. For the other atmospheres, however, equilibrium conditions had to be maintained throughout, because reversibility was observed.

Nitric oxide, purified as described, has a negligible effect on the diodes. Less carefully purified nitric oxide caused a definite channel, which we ascribe to the presence of traces of nitrogen peroxide.

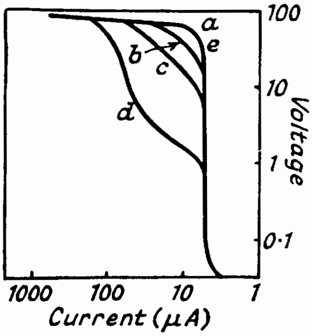
Nitrogen peroxide and bromine were used in succession. Nitrogen peroxide was allowed into the manifold; the non-chemisorbed gas was pumped off, the characteristics were observed, and the experiment was then repeated for a higher initial pressure of nitrogen peroxide. Air was allowed into the apparatus, the system was again evacuated, and the bromine was introduced. Curves of the type shown in Fig. 7 were obtained for such a cycle. It can be seen that both reagents produce channels whose magnitude depends on the initial concentration of the gas; further, both reagents slightly raise the voltage at which breakdown occurs.

FIG. 7. *Reverse characteristics for the nitrogen peroxide–moist air–bromine cycle.*



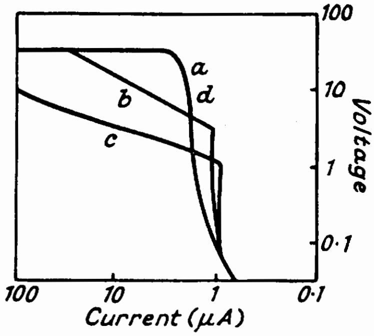
*a, Initial characteristic. b,* $NO_2$ *admitted from source at* −80° *and pumped off. c,* $NO_2$ *admitted from source at room temp. and pumped off. d, Moist air admitted and pumped off. e,* Br *admitted from source at* −180° *and pumped off. f,* Br *admitted from source at room temp. and pumped off.*

FIG. 8. *Reverse characteristics showing the reversible leakage effect induced by water vapour.*



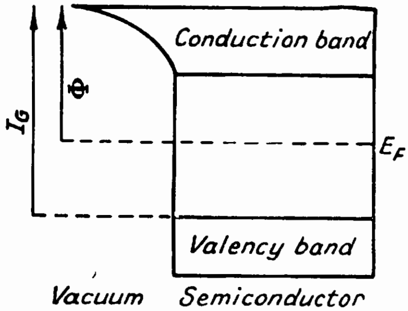
*a, Initial characteristic. b–d, Water vapour admitted to a pressure of* (*b*) 1·5, (*c*) 4, *and* (*d*) 10 *mm.* Hg. (*e*) *Water vapour pumped off.*

FIG. 9. *Reverse characteristics showing the reversible "anti-channel" effect of water vapour combined with leakage effects.*



*a, Initial characteristic. b, c, Water vapour admitted at* (*b*) 2, (*c*) 6 *mm.* Hg. *d, Water vapour pumped off.*

FIG. 10. *Energy levels of a semiconductor.*



Iodine behaves similarly to bromine, with regard to both channel formation and raising of the breakdown voltage.

With originally channel-free diodes, water gives no apparent new channels under our experimental conditions, but a reversible leakage effect resulting in a family of curves of type *B* (Fig. 8). If a channel, of unknown origin, resulting from incorrect surface treatment, is initially present, and the diode is exposed to water vapour, some of the channel is cancelled (Fig. 9) while the upper part of the curve becomes of type *B*. For a very large initial channel it becomes difficult to distinguish between the various types of phenomena. In addition to these effects a large pressure of water vapour lowers the breakdown voltage.

The failure of water vapour to cause *n*-type channels to appear on the *p* side of our (alloy) junctions does not conflict with the findings of Brown[7] and others,[8, 9] and is due to the very heavy doping of our *p*-type material (estimated to be of the order of $10^{19}$ indium atoms per $\text{cm.}^3$). The " grown " junctions upon which water has been shown to induce channels were made with *p*-type material of acceptor density about $10^{15}$ $\text{cm.}^{-3}$.

Sulphur dioxide behaves similarly to water in that it cancels channels and gives a family of curves of type *B*. In addition, there is a tendency to raise the breakdown voltage.

Anhydrous ammonia behaves similarly to water and sulphur dioxide, except that the breakdown voltage seems to be completely unaffected.

## DISCUSSION

It seems probable, from the similarity between our observations on bromine and nitrogen peroxide, and those of Christensen[9] on oxygen, that oxidation is responsible for the channel effects observed. This implies that attack by neutral atoms or molecules can result in channel formation. An electron-transfer reaction must therefore be postulated at the semiconductor surface, such as that represented by eqn. (2) for *p*-type channel formation:

$$\text{X (on surface)} + \text{Surface} \overset{+}{\underset{-}{\rightleftharpoons}} \text{X}^- \text{ (on surface)} + \text{Surface}^+ \quad . \quad . \quad (2)$$

where X is the adsorbate and Surface$^+$ indicates an excess of positive holes at the surface. This equation, which we have deduced directly from the accepted mechanism of channel formation[5, 7] is in agreement with Dowden's model of chemisorption.[2]

The equilibrium constant for this reaction is given by:

$$K = \frac{[\text{X}^-][\text{positive holes at surface}]}{[\text{X}][\text{electrons at surface}]}$$

The quantity [X] will be determined by the appropriate isotherm, which in the simplest case could be the Langmuir isotherm:

$$n/N_0 = \theta = kp/(\nu + kp)$$

where $n$ = number of molecules adsorbed, $N_0$ = number of molecules in the complete monolayer, $k = 10^{22} \times 3{\cdot}5\gamma/\sqrt{(MT)}$, $\gamma$ = fraction of molecules which condense on striking, $\nu$ = rate of evaporation, $M$ = molecular weight of the gas, and $T$ = absolute temperature.

The electron-transfer reaction may be considered to produce a homogeneous electronic equilibrium whose equilibrium constant is governed by the relation

$$-\Delta G = \boldsymbol{R}T \ln K$$

where the standard states are given as 1 mole of $\text{X}^-$ (containing $\boldsymbol{N}$ electrons where $\boldsymbol{N}$ is Avogadro's number), 1 mole of X, $\boldsymbol{N}$ electrons at the surface and $\boldsymbol{N}$ holes at the surface. There must be no movement of atoms or molecules into or out of the surface. In such a case an estimation of $-\Delta G$ can be made in terms of the electron affinity of X and the work function of the semiconductor, which will determine the distribution of the electron " gas " between X and the surface.

The electron affinity ($\alpha$) of X is defined as the energy liberated when an electron is put into the neutral molecule. This will be the energy change occurring when an electron is brought from infinity into the lowest unoccupied orbital of X. The isothermal work function ($\Phi$) of a solid is usually defined as the energy required to move an electron from the Fermi level $E_F$ to infinity (Fig. 10), whereas the adiabatic work function $I_G$ would be measured from the top of the valency band. Since experimental conditions are usually isothermal $\Phi$ will apply. This uncertainty regarding the level from which to measure the energy does not arise in the case of the adsorbate, X, because atoms and molecules undergo no appreciable excitation from bonding to antibonding orbitals at room temperature.

The change in free energy in going from reactants to products must be given by $\Phi - \alpha$, in which case

$$-(\Phi - \alpha)N = RT \ln K_-$$

It can be seen that if $\alpha$ is large there will be considerable channel formation; further, if [X] becomes large because the gas pressure is increased there will again be an increase in channel formation. From a knowledge of [X] (*via* the appropriate isotherm) and of the free-energy change it becomes possible to estimate the number of negative ions which have been formed on the surface.

A similar treatment can be applied to the electron-transfer reaction (3) which would give an *n*-type channel on the *p* side:

$$\mathrm{X} + \mathrm{Surface}^{\pm} \rightleftharpoons \mathrm{X}^{+} + \mathrm{Surface}^{-} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which case the free energy change is given by $\beta - \Phi$, and

$$-(\beta - \Phi)N = RT \ln K_+$$

where $\beta$ is the ionisation potential of X. If $\beta$ is large compared with $\Phi$ there will be little chemisorption, and consequently slight channel formation. We have in fact found no evidence of *n*-type channel formation by nitric oxide, in spite of the known stable existence of the nitrosonium ion $NO^+$, in agreement with expectations from published values for its ionisation potential. This is given [11] as 9·5 ev which is much higher than the work function [12] of germanium, 4·8 ev, giving a very small stability constant for reaction (3). The adsorption isotherms of the adsorbates discussed must be determined before the validity of these equations can be fully tested by comparing the electron affinities (or ionisation potentials) and surface concentrations of adsorbates with their channel-forming powers. It has however been observed that the effect of halogens is much greater than that of nitrogen peroxide. This is to be expected from these considerations, since the halogens have a much larger electron-affinity than nitrogen peroxide.

The similarity in the results obtained by using water, sulphur dioxide, or ammonia suggests that ionising solvents are responsible for the production of curves of type *B* (Fig. 2). It is possible that these merely solvate the ions which are present on the surface, as implied by Law.[3] If such ions are also responsible for channel formation, solvation would automatically reduce the electrostatic effect of the negative or positive ions, which maintain, respectively, the positive or negative space-charge in the vicinity of the surface, because each ion becomes surrounded by a sheath of solvent molecules which effectively screen its charge in addition to increasing its distance from the germanium surface. This mechanism could therefore explain the cancellation of channels by ionising solvents which we have observed (see Fig. 9). Complete removal of the solvent usually results in the reappearance of the channel, which is also not unexpected on the basis of this solvation mechanism. The irreversible removal of the nitrogen peroxide channel by moist air, reported here, is however difficult to explain in these simple terms, and probably involves chemical reaction between the chemisorbed nitrogen peroxide and the adsorbed water.

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[11] Tate, Smith, and Vaughan, *Phys. Rev.*, 1935, **48**, 525; Hagstrum and Tate, *ibid.*, 1941, **59**, 354.

[12] Wright, *Proc. Inst. El. Engineers*, 1953, **100**, 111, 125; Law, *J. Phys. Chem.*, 1955, **59**, 543.