PHYSICAL REVIEW B VOLUME 25, NUMBER 7 1 APRIL 1982

Formation of H^- ions by backscattering thermal hydrogen atoms from a cesium surface

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(Received 1 October 1981)

We have investigated the formation of negative hydrogen ions by backscattering thermal hydrogen atoms incident on a thick cesium surface. The incident hydrogen atoms are produced by thermal dissociation of molecular hydrogen at temperatures of about 2500 K. The negative ions are produced with an efficiency of 10^{-4} ions per incident atom. Our data show that the backscattering theory of Hiskes-Gardner-Karo, originally developed for incident hydrogen atoms with energies above 100 eV, can be extrapolated down to the 1-eV range. One way of comparing our experimental results with the above theory is to determine the average survival probability for the negative hydrogen ions as they leave the cesium surface. We obtain a survival probability of 0.005 for hydrogen from a 2500-K oven, in close agreement with the value of 0.004 calculated by extrapolating the experimental results of Hiskes and Schneider down to 1 eV. In addition to the negative hydrogen ions we see electrons produced with efficiencies about one hundred times greater than for the negative ions. The electrons appear to be produced by an Auger process accompanying a chemical reaction of hydrogen with cesium.

I. INTRODUCTION

There has been some interest in the reflection of atomic hydrogen from alkali surfaces as a possible mechanism for producing negative hydrogen ions. The production of negative hydrogen ions by backscattering protons in the 100-eV energy range from a cesiated tungsten surface was investigated theoretically by Hiskes, Karo, and Gardner.[1,2] Using two experimentally determined parameters, Hiskes and Schneider fitted the backscattering theory to their experimental data for protons with energies from 150 eV to 5 keV incident on alkali surfaces.[3]

We have observed the creation of both negative hydrogen ions and electrons when thermal hydrogen atoms are incident on a thick layer of cesium. The existence of negative hydrogen ions due to thermal hydrogen atoms hitting a cesiated surface was first reported by Graham.[4] Our data for the absolute production yields of negative hydrogen ions shows that the backscattering theory[1,2] can be extrapolated down to the 1-eV range. The same parameters obtained from the experimental data of Hiskes and Schneider[3] can be used to fit the backscattering theory to our data.

In addition to the emission of negative hydrogen ions, we observe electron emission which appears to be due to a chemical reaction of atomic hydrogen with cesium. Electron emission accompanying chemical reactions has been occasionally reported in the literature. Haber and Just[5] were among the first to observe electron emission when water vapor or chlorine gas reacted with alkali metal surfaces. More recently, Kasemo and Wallden[6] observed the emission of both electrons and photons when halogen gases reacted with a sodium surface. Trowbridge and Herschbach[7] have measured the emission of electrons and positive and negative ions when halogen gases reacted with alkali-metal surfaces. It appears that the electrons are emitted by an Auger process accompanying chemical reactions at the surface.[8,9]

II. EXPERIMENTAL APPARATUS

The central part of the experiment is an approximately planar diode shown in Fig. 1. The anode of the diode consists of $2\times40\text{-mm}^2$ molybdenum ribbons forming a 3-mm-wide extraction slot.

The cathode of the diode is a $2.5\times2\text{-cm}^2$ molybdenum base plate mounted onto a cooling block whose temperature can be maintained from $+20$ to $-85\,^{\circ}\mathrm{C}$ using refrigerated methanol as coolant. On top of the base plate are two stainless steel wedges used to focus the beam of H^- ions and electrons which are created at the cathode and extracted through the anode slot.

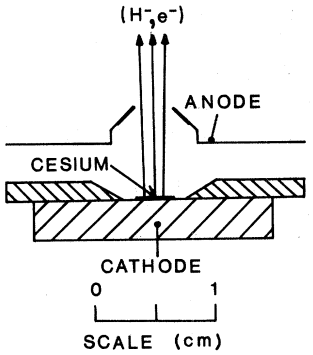

FIG. 1. Schematic diagram of the vacuum diode.

The anode of the diode is grounded and the cathode is negatively biased at -5 kV. The diode current is collected by the "cathode cup" which is a Faraday cup located behind the anode. This cup is positively biased at $+500$ V to retain secondary electrons generated by incoming electrons and H^- ions.

Fig. 2 shows the experimental setup for measuring the fractions of the electrons and ions in the extracted beam. About 1% of the beam exits through a small opening in the back of the cathode cup and is intercepted by the "ion cup," another Faraday cup about 20 cm behind the cathode cup. A transverse magnetic field of 10 to 20 G applied along the path between the two cups deflects the electrons out of the beam path so that only ions hit the ion cup. This enables us to measure the ratio of electrons to ions in the extracted beam. About 1% of the beam reaching the ion cup exits through a small slot in the rear of the ion cup and is mass analyzed by a magnetic sector mass spectrometer. This enables us to determine which ion species have been emitted from the cathode. The relative yield of a particular ion is obtained from the mass spectra. In order to obtain the absolute yield of a particular ion species, the relative yield is multiplied by the ratio $J_k/\phi(\mathrm{H})$, where J_k is the total current density of electrons and all negative ions extracted from the cathode and $\phi(\mathrm{H})$ is the atomic hydrogen flux produced in a tungsten oven and then directed onto the cathode.

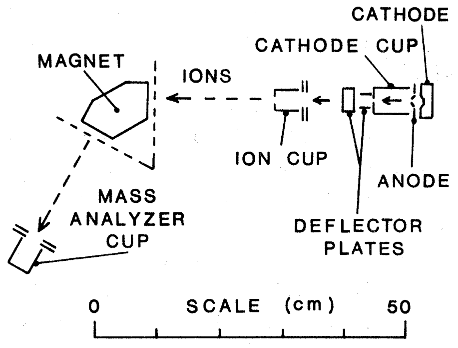

FIG. 2. Experimental setup for measuring secondary emission yields.

The vacuum system was evacuated by a six-inch oil diffusion pump and liquid nitrogen trap to a background pressure in the 10^{-8}-Torr range, measured with a Veeco RG-840 ionization gauge. A Veeco SPI-10 Residual Gas Analyzer showed this background pressure to be predominantly water vapor.

In order to reduce the work function of the cathode, cesium vapor is produced in a small oven and directed onto the surface of the cathode by means of a heated feeder tube. The cesium oven is a stainless steel chamber into which is placed a glass ampoule containing 2 g of cesium. After the oven has been evacuated, the ampoule is crushed using a plunger mounted onto the oven with bellows. A typical cesium atom flux at the cathode is $\phi(\mathrm{Cs}) = 10^{15}$ at. cm^{-2} s^{-1} for an oven temperature of 150 °C. When the cathode temperature is lower than a critical temperature T_{cr}, the cesium atoms condense on the surface of the cathode with a sticking probability close to unity and a thick cesium film builds up, lowering the work function of the cathode to about 1.9 eV. The observed critical temperature agrees well with the formula

$$T_{\mathrm{cr}} = 3840/[27.37 - \log_{10}\phi(\mathrm{Cs})] ,$$

which is obtained from Eq. (51) of Ref. 10. The temperature is in K and the flux is in at. cm^{-2} s^{-1}.

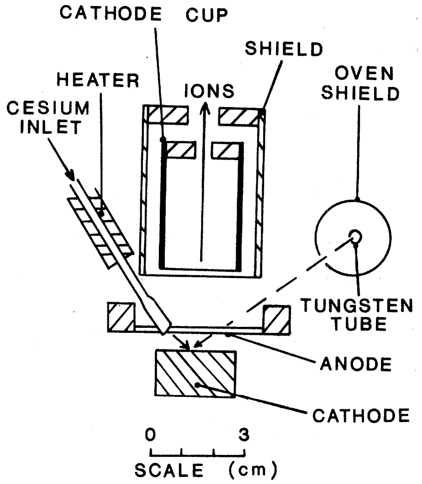

FIG. 3. View of the vacuum diode with location of cesium feeder tube and hydrogen oven.

For $\phi(\text{Cs})=10^{15}$ at. cm^{-2} s^{-1}, $T_{\text{cr}}=37\,^{\circ}\text{C}$. We kept the cathode cooled to $-50\,^{\circ}\text{C}$, well below this critical temperature. The cesium flux used was about 2 orders-of-magnitude larger than the flux of residual water vapor so that we would not have our results affected by the presence of CsOH. The orientation of the feeder tube from the cesium oven with respect to the cathode is shown in Fig. 3. The feeder tube is heated to about 300 °C so that $\phi(\text{Cs})$ can be controlled by varying only the temperature of the cesium oven.

Also shown in Fig. 3 is the position of the hydrogen oven, used to produce and direct a beam of atomic hydrogen onto the cathode. The atomic hydrogen is produced by thermal dissociation of hydrogen gas in a tungsten tube of 3.2-mm diameter heated to 2500 K by electron bombardment. The H and residual H_2 effuses from a 0.7-mm diameter hole in the side of the tungsten tube onto the cathode.

The hydrogen atoms may be considered to effuse from the exit hole in the tungsten tube if the collisional mean free path λ is larger than the exit hole diameter.[11–13] In order for the H atoms to be in equilibrium with the H_2 molecules, λ must be smaller than the inner diameter of the tungsten tube. This requires a H_2 pressure inside the tube to be on the order of 0.1 to 1 Torr. Considering the pumping speed of our diffusion pump through the refrigerated baffles, the measured pressure in the vacuum chamber $P(H_2)$ must be on the order of 10^{-5} to 10^{-4} Torr.

We have calculated the atomic hydrogen flux at the surface of the cathode as a function of chamber pressure $P(H_2)$ and tungsten tube temperature T. The temperature T was measured with a Leeds and Northrop 8622-C optical pyrometer. The effusion of hydrogen atoms from our tungsten oven can be obtained from kinetic theory.[12] For the geometry shown in Fig. 3, the flux of hydrogen atoms is

$$\phi(\text{H})=0.118n(\text{H})T^{1/2} \tag{1}$$

with $\phi(\text{H})$, $n(\text{H})$, and T in atoms cm^{-2} s^{-1}, cm^{-3}, and K, respectively. The atomic hydrogen density in the oven $n(\text{H})$ is determined by equating the flux of particles effusing out of the oven with the flux of molecular hydrogen pumped out of the system

$$\tfrac{1}{4}A[\tfrac{1}{2}n(\text{H})\langle v(\text{H})\rangle_{\text{av}}+n(\text{H}_2)\langle v(\text{H}_2)\rangle_{\text{av}}]=Sn' , \tag{2}$$

where A is the exit hole area in the tungsten tube, S is the pumping speed of our diffusion pump with baffles, and n' is the molecular hydrogen density in the vacuum chamber. The atomic and molecular hydrogen pressures inside the oven are determined by the dissociation reaction for H_2

$$K(T)=P(\text{H})/[P(\text{H}_2)]^{1/2} , \tag{3}$$

where the equilibrium constant $K(T)$ is given in the JANAF tables[14] and $P(\text{H})$ and $P(\text{H}_2)$ are given in atmospheres. Using Eqs. (2), (3), and the relation $P=nkT$ we can solve for the atomic hydrogen density in the oven

$$n(\text{H})=[-1+(1+4\alpha\beta)^{1/2}]/2\alpha , \tag{4}$$

where $\alpha=1.932\times10^{-22}T/K(T)$ cm^3 and $\beta=6.47\times10^{21}P(\text{H}_2)/T^{1/2}$ cm^{-3} with $n(\text{H})$, T and $P(\text{H}_2)$ in cm^{-3}, K and Torr, respectively. Inserting this $n(\text{H})$ into Eq. (1) we calculate $\phi(\text{H})$. As an example, for $T=2500$ K and $P(\text{H}_2)=10^{-5}$ Torr, we calculate $\phi(\text{H})\sim10^{16}$ at. cm^{-2} s^{-1} for the flux incident on the cathode.

III. EXPERIMENTAL RESULTS AND DISCUSSION

We observe the production of H^- ions and electrons when atomic hydrogen is directed onto the refrigerated cathode which is coated with cesium. Typically, the incident cesium flux is 10^{15} at. cm^{-2} s^{-1}, the hydrogen oven temperature is 2350 K, the chamber pressure is 10^{-4} Torr of molecular hydrogen, and the atomic hydrogen flux is 10^{16} at. cm^{-2} s^{-1}.

Experimentally, it is observed that there are two requirements for the production of H^- ions; the cathode must be covered with cesium and the hydrogen interacting with the cesium surface must be atomic. For example, when the cathode was bare molybdenum, no H^- ions were observed when either molecular or atomic hydrogen was directed onto the cathode. Similarly, no H^- ions were observed when the cathode was coated with cesium but the hydrogen oven was either cold or no hydrogen gas was admitted. The current density of H^- ions $J(H^-)$ increases linearly with atomic hydrogen flux $\phi(\text{H})$, as shown by the lower curve in Fig. 4.

The upper curve in Fig. 4 is the observed electron current density. The electron current does not increase linearly with $\phi(\text{H})$ but more slowly. As with the production of H^- ions, the electron emission also requires atomic hydrogen incident on the

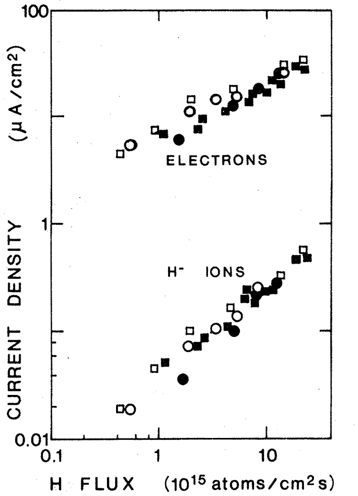

FIG. 4. Current density at cathode of backscattered H$^-$ ions and of exoelectrons as a function of the flux of hydrogen atoms. $\phi(\text{Cs})=10^{15}\ \text{cm}^{-2}\,\text{s}^{-1}$.

cathode. Some photoelectrons were produced because radiation from the hydrogen oven was incident on the cesium surface. The photoelectron current can be measured by keeping the hydrogen oven hot but not letting in hydrogen gas. Even for a 2500-K oven, the photoelectron current density was less than 1 $\mu\text{A}\,\text{cm}^{-2}$. For the lower oven temperatures typically used, the photoelectron current became negligible.

The electrons are probably emitted by an Auger process accompanying the adsorption of hydrogen atoms on the cesium surface. The Auger mechanism would involve the tunneling of an electron from the cesium metal to the adsorbed hydrogen atom.[9] During this tunneling process a photon is emitted which can be absorbed by another electron in the cesium metal which escapes from the surface if its excitation energy exceeds 1.9 eV, the work function of cesium. Although the above Auger process would indicate the electron emission to depend linearly on the atomic hydrogen flux, our data in Fig. 4 shows this dependence to be less than linear. However, the work of Papageorgopoulos and Chen[15] indicates that the work function of 1.9 eV for pure cesium increases to about 2.3 eV for cesium with adsorbed hydrogen. Although the emission of electrons due to chemical reactions (exoelectrons) has been studied by many authors, we are not aware of any specific observation of electron emission accompanying adsorption of hydrogen on cesium. On the other hand, electron emission has been observed when halogen gases were adsorbed on sodium[6,7] and for oxygen adsorbed on magnesium.[16] In these works, the electron emission is also attributed to an Auger process.

In contrast to the electron emission process involving the adsorption of hydrogen atoms onto the cesium surface, the production of H$^-$ ions is most likely due to the reflection of hydrogen atoms from the cesium surface. This effect was first observed by Graham in a similar experiment.[4] Hiskes *et al.*[1,2] has developed a theory for the reflection from alkali-metal surfaces of hydrogen ions with incident energies greater than 10 eV. According to that theory, the reflected hydrogen emerges as a positive ion which can be Auger neutralized near the surface, and then converted to an H$^-$ ion by the capture of another electron from the cesium metal. The probability for this process is called the formation probability. The probability that the H$^-$ ion will survive as it moves away from the cesium surface is called the survival probability. The product of these two probabilities is proportional to the production probability, defined as the number of H$^-$ ions produced per incident hydrogen atom. The theoretical production efficiency is given by Eq. (7) of the paper by Hiskes and Schneider[3]

$$\frac{J(\text{H}^-)}{J(\text{H}^0)}=2\int\int f_i(v)\cos\theta[1-\exp(-\alpha/v\cos\theta)]\exp(-\beta/v\cos\theta)d(\cos\theta)dv\ . \tag{5}$$

Here $f_i(v)$ is the distribution of the exiting ions that we shall take equal to the incident distribution:

$$f_i(v)=2(v^3/v_t^4)\exp(-v^2/v_t^2)\ ,$$

with $v_t=(2kT/m)^{1/2}$ where T is the temperature of the hydrogen oven. θ is the angle of the backscattered ions measured from the normal. The parameters $\alpha=0.39$ and $\beta=0.48$ are taken from Hiskes and Schneider,[3] where α and β are normalized so that the velocity of a 200-eV hydrogen atom is unity. In Eq. (5) the term $1-\exp(-\alpha/v\cos\theta)$ is the formation probability of the H$^-$ ion and the term $\exp(-\beta/v\cos\theta)$ is the survival probability.

The integration over velocity in Eq. (5) is taken for all H atoms incident on the cathode with kinetic energies greater than the difference of the work function for cesium ($W=1.9$ eV) and the electron

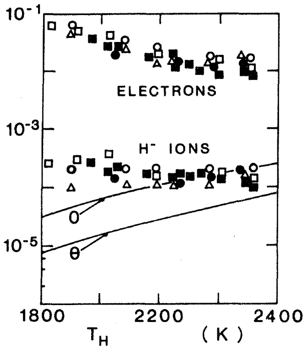

FIG. 5. Production efficiency (number of particles per incident hydrogen atom) of H^- ions and electrons as a function of hydrogen oven temperature. The two solid curves are plots of Eq. (5) for $\theta=0$ in the top curve and for integration over angle θ in the bottom curve. $\phi(\mathrm{Cs})=10^{15}\ \mathrm{cm^{-2}\,s^{-1}}$.

affinity for hydrogen ($A=0.75$ eV),

$$\tfrac{1}{2}mv^2 \geq W-A=1.15\ \mathrm{eV}\ . \qquad (6)$$

Equation (5), corresponding to H^- ions leaving the surface at all angles, is plotted as the lower curve in Fig. 5. The experimentally measured production efficiency of H^- ions is shown for different hydrogen fluxes. Our experimental data agrees better with the upper curve where Eq.(5) is plotted for $\theta=0$. It is not clear why the agreement is not too good for low temperatures, but at 2500 K the measured value of 1.15×10^{-4} for the efficiency is quite close to the theoretical value of 2×10^{-4}.

An alternative way to compare our measurements with Hiskes's theory is to determine the average survival probability from our data. This can be calculated by dividing the formation efficiency of H^- ions $\eta(H^-)$ by the fraction of hydrogen atoms in the tail of the Maxwellian distribution $F(T)$, having energies above 1.15 eV, giving the average survival probability

$$\langle \exp(-\beta/v)\rangle_{\mathrm{av}}=\eta(H^-)/F(T)\ , \qquad (7)$$

where $\eta(H^-)$ is our measured formation efficiency plotted in Fig. 5. As a sample calculation, consider the formation of H^- ions when hydrogen atoms from a 2500-K oven are incident on a cesium surface. From Fig. 5 we get $\eta(H^-)\sim1.5\times10^{-4}$ and for a Maxwellian distribution we get

$$F(T)=2\int x^3\exp(-x^2)dx=0.31\ .$$

This gives $\langle \exp(-\beta/v)\rangle_{\mathrm{av}}\simeq0.005$ from Eq. (7). Because the survival probability depends exponentially on the velocity, about half of all the surviving H^- ions have energies greater than 1.5 eV. Using the same value for β obtained from the work of Hiskes and Schneider gives a survival probability of 0.004 for 1.5-eV H^- ions which is close to our observed value of 0.005. This indicates that the backscattering theory can be extrapolated to 1-eV energies so that β is valid for energies from 1 to 5000 eV.

The production of H^- ions when $H_2{}^+$ ions are incident on nonalkali metals was studied by Verbeek, Eckstein, and Bhattacharya.[17] They used $H_2{}^+$ ions in the energy range of 5 to 16 keV, which is about four orders of magnitudes greater than the energies used by us. They also consider the possibility that the H^- ions are produced by a reflection process as described by Hiskes. They measure H^- ions when the $H_2{}^+$ ions are incident on metal surfaces with large work functions, such as gold and molybdenum. In our case, hydrogen atoms with energies of about 1 eV are reflected as H^- ions only from a surface with a low work function, specifically a cesium surface.

IV. CONCLUSION

We have observed the production of both negative hydrogen ions and electrons when hydrogen atoms from a hot tungsten oven are directed onto a cesium surface. As an example, for atoms from a 2500-K oven, the efficiency of producing negative hydrogen ions is about 1.5×10^{-4} ions per incident hydrogen atom. Because of the surface barrier of about 1 eV, only atoms in the tail of the Maxwellian distribution can be reflected. When the work function of the cathode was increased by removing the cesium, no negative hydrogen ions were seen. For a cesium surface, we obtain an average probability of about 0.005 that the negative hydrogen ions will survive as they leave the surface. This compares favorably with the value of 0.004 calculated by extrapolating the experimental results of Hiskes and Schneider from the 100-eV range down to the 1-eV range. This indicates that the backscattering theory of Hiskes-Karo-Gardner is valid for incident hydrogen atoms with energies in the $(1-5000)$-eV range.

The efficiency of producing electrons is about 0.01 electrons per incident hydrogen atom which is about 100 times the efficiency to produce negative hydrogen ions. The electron emission appears to be an Auger process due to the reaction of hydrogen atoms with the cesium surface. The photoelectrons were only about 10% of the total electron current for a 2500-K oven and an incident atomic hydrogen flux of about 10^{16} at. cm^{-2} s^{-1}. For lower oven temperatures the photoelectron current became negligible.

ACKNOWLEDGMENTS

We would like to thank Dr. John Hiskes for several useful discussions, J. Greer for building the hydrogen oven, and E. Hartford and G. Wirth for building most of the remaining experimental apparatus. This research was partially supported by the National Science Foundation.

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