Bright hydrogen-light source due to a resonant energy transfer with strontium and argon ions

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New Journal of Physics 4 (2002) 70.1–70.28 (http://www.njp.org/)
Received 13 August 2002
Published 2 October 2002

Abstract. A plasma called a resonant transfer (rt) plasma formed with a low field (1 V cm\(^{-1}\)), at low temperatures (e.g. \(\approx 10^3\) K), from atomic hydrogen generated at a tungsten filament and strontium which was vapourized by heating the metal. Strong vacuum ultraviolet emission was observed that increased with the addition of argon, but not when sodium, magnesium or barium replaced strontium or with hydrogen, argon or strontium alone. Characteristic strontium and argon emission was observed which supported a resonant-energy-transfer mechanism. Significant Balmer \(\alpha\) line broadening corresponding to an average hydrogen atom temperature of 14, 24, and 23–45 eV was observed for strontium and argon–strontium rt plasmas and discharges of strontium–hydrogen, helium–hydrogen, argon–hydrogen, strontium–helium–hydrogen and strontium–argon–hydrogen, respectively, compared to \(\approx 3\) eV for pure hydrogen, krypton–hydrogen, xenon–hydrogen and magnesium–hydrogen. To achieve that same optically measured light output power, hydrogen–sodium, hydrogen–magnesium and hydrogen–barium mixtures required 4000, 7000 and 6500 times the power of the hydrogen–strontium mixture, respectively, and the addition of argon increased these ratios by a factor of about two. A glow discharge plasma formed for hydrogen–strontium mixtures at an extremely low voltage of about 2 V compared to 250 V for hydrogen alone and sodium–hydrogen mixtures, and 140–150 V for hydrogen–magnesium and hydrogen–barium mixtures.

1. Introduction

Suitable hydrogen plasma light sources and spectrometers have been developed which permit observations in the vacuum ultraviolet (VUV). Developed sources that provide a suitable intensity are high voltage glow discharges, synchrotron devices, inductively coupled plasma generators [1] and magnetically confined plasmas. Glow discharge devices have been developed over the
decades as light sources, ionization sources for mass spectroscopy, excitation sources for optical spectroscopy and sources of ions for surface etching and chemistry [2]–[4]. A Grimm-type glow discharge is a well established excitation source for the analysis of conducting solid samples by optical emission spectroscopy [5]–[7]. Despite extensive performance characterizations, data was lacking on the plasma parameters of these devices. Kuraica and Konjevic [8] and Videnovic et al [9] have characterized these plasmas by determining the excited hydrogen atom concentrations and energies from measurements of the line broadening of the 656.3 nm Balmer \( \alpha \) line. The data was analysed in terms of external Stark and Doppler effects wherein acceleration of charges such as \( \text{H}^+ \), \( \text{H}_2^+ \) and \( \text{H}_3^+ \) in the high fields (e.g. over 10 kV cm\(^{-1}\)) which were present in the cathode fall region was used to explain the Doppler component.

More recently, microhollow glow discharges have been spectroscopically studied as candidates for the development of an intense monochromatic VUV light source (e.g. Lyman \( \alpha \)) for short wavelength lithograph for production of the next generation of integrated circuits. A neon–hydrogen microhollow cathode glow discharge has been proposed as a source of predominantly Lyman \( \alpha \) radiation. Kurunczi et al [10] observed intense emission of Lyman \( \alpha \) and Lyman \( \beta \) radiation at 121.6 and 102.5 nm, respectively, from microhollow cathode discharges in high-pressure Ne (740 Torr) with the addition of a small amount of hydrogen (up to 3 Torr). With essentially no molecular emission observed, Kurunczi et al attributed the anomalous Lyman \( \alpha \) emission to the near-resonant energy transfer between the \( \text{Ne}_2^* \) excimer and \( \text{H}_2 \), which leads to formation of \( \text{H}(n = 2) \) atoms, and attributed the Lyman \( \beta \) emission to the near-resonant energy transfer between excited \( \text{Ne}^* \) atoms (or vibrationally excited neon excimer molecules) and \( \text{H}_2 \), which leads to formation of \( \text{H}(n = 3) \) atoms. Despite the emission characterization of this source, data is lacking about plasma parameters.

For analyses of solids, direct current (dc) glow discharge sources have been successfully complemented by radio-frequency (rf) discharges [11]. The use of dc discharges is limited to metals, whereas rf discharges are applicable to non-conducting materials. Other developed sources that provide a usefully intense plasma are synchrotron devices, inductively coupled plasma generators [12] and magnetically confined plasmas. Plasma characterization data on these sources is also limited.

A new plasma source has been developed that operates by incandescently heating a hydrogen dissociator and a catalyst to provide atomic hydrogen and gaseous catalyst, respectively, such that the catalyst reacts with atomic hydrogen to produce a plasma called a resonant transfer (rt) plasma. The plasma forms by a rt mechanism involving the species providing a net enthalpy of a multiple of 27.2 eV and atomic hydrogen. It was extraordinary that intense VUV emission was observed [13]–[20] at low temperatures (e.g. \( \approx 10^3 \) K) from atomic hydrogen and certain atomized elements or certain gaseous ions which singly or multiply ionize at integer multiples of the potential energy of atomic hydrogen, 27.2 eV, that comprise catalysts. The only pure elements that were observed to emit VUV were those wherein the ionization of \( t \) electrons from an atom to a continuum energy level is such that the sum of the ionization energies of the \( t \) electrons is approximately \( m \times 27.2 \) eV, where \( t \) and \( m \) are each an integer (e.g. K, Cs, Sr, Sr\(^+ \) and Rb\(^+ \) each ionize at integer multiples of the potential energy of atomic hydrogen and caused emission, whereas the chemically similar atoms, Na, Mg and Ba, do not ionize at integer multiples of the potential energy of atomic hydrogen and caused no emission). The theory has been given previously [16, 20, 21].

He\(^+ \) ionizes at 54.417 eV, which is \( 2 \times 27.2 \) eV. While the ionization energy of Ar\(^+ \) to Ar\(^{2+} \) is 27.6 eV [22] and the ionization of Sr\(^+ \) to Sr\(^{3+} \) has a net enthalpy of reaction of 53.92 eV [22], an
The electric field may adjust the energy of ionizing Ar$^+$ to Ar$^{2+}$ and Sr$^+$ to Sr$^{3+}$ to match the energy of 27.2 and $2 \times 27.2$ eV, respectively. It was reported previously that characteristic emission was observed from a continuum state of Ar$^{2+}$ at 45.6 nm without the typical Rydberg series of Ar I and Ar II lines which confirmed the resonant nonradiative energy transfer of 27.2 eV from atomic hydrogen to Ar$^+$ [14]. Predicted emission lines were observed from helium–hydrogen [20, 21] as well as strontium–argon–hydrogen plasmas [14] that supported the rt plasma mechanism.

To further characterize strontium and argon–strontium rt plasmas and the catalyst mechanism, plasma formation studies, VUV spectroscopy, broadening of the Balmer $\alpha$ line and optical power balance measurements were performed relative to mixtures of hydrogen and chemically similar controls that do not have electron ionization energies which are a multiple of 27.2 eV. Four different light sources were used to form and characterize the rt plasmas under a range of plasma conditions. A type I light source shown in figure 1 comprised a tungsten filament to heat and vapourize some strontium as a source of catalyst and to dissociate molecular hydrogen to atomic hydrogen. A type II light source shown in figure 2 comprised a microwave discharge cell which provided standard emission spectra of hydrogen and argon. A type III light source shown in figure 3 comprised a dc glow discharge cell which formed gaseous catalyst such as Ar$^+$, Sr$^+$ and atomic hydrogen. A type IV light source shown in figure 4 comprised a dc glow discharge that was operated at a temperature sufficient to vapourize some strontium as a source of catalyst. The glow discharge provided some atomic hydrogen as well and the catalytic reaction was anticipated to maintain the plasma at extraordinarily low voltages and input powers. The addition of argon to the plasma further provided the catalyst Ar$^+$.

Since a conventional discharge power source was not present in the type I light source, the formation of a plasma would require an energetic reaction. The observation of Ar$^{2+}$ or Sr$^{3+}$ emission would serve as substantial evidence of the energy transfer from atomic hydrogen since there is no conventional mechanism which would explain this emission,
Figure 2. The experimental set-up of a type II light source comprising a microwave plasma cell and a VUV spectrometer which was differentially pumped.

and the net enthalpy of the corresponding reactions matches one and two times 27.2 eV, respectively, the condition to be an rt plasma catalyst in each case. The origin of Doppler broadening is the relative thermal motion of the emitter with respect to the observer—in this case the spectrometer. The observation of a high hydrogen temperature with no conventional explanation would indicate that an rt plasma must have a source of free energy. Since line broadening is a measure of the atom temperature, and a significant increase was expected for catalysts, strontium or argon with hydrogen, the power balance of a gas cell having vapourized strontium and atomized hydrogen from pure hydrogen or argon–hydrogen mixture (77/23%) was measured by integrating the total light output corrected for spectrometer system response and energy over the visible range. We report the results of these characterizations in section 3 and discuss the implications regarding the rt plasma mechanism in section 4. Section 5 gives a summary.

2. Experimental details

2.1. VUV spectroscopy

Due to the short wavelength of this radiation, ‘transparent’ optics do not exist for VUV spectroscopy. Therefore, a windowless arrangement was used wherein the source was connected to the same vacuum vessel as the grating and detectors of the VUV spectrometer. Windowless VUV spectroscopy was performed with a VUV spectrometer that was mated with the cell.

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Figure 3. Cylindrical stainless steel cell comprising a type III light source for studies of the broadening of the Balmer α line emitted from gas discharge plasmas of pure hydrogen alone or with strontium or magnesium or a mixture of 10% hydrogen and helium, argon, krypton or xenon.

Differential pumping permitted a high pressure in the cell as compared to that in the spectrometer. This was achieved by pumping on the cell outlet and pumping on the grating side of the collimator that served as a pinhole inlet to the optics. The cell was operated under gas flow conditions while maintaining a constant gas pressure in the cell. The gas pressure inside the cell was maintained at about 300 mTorr with a hydrogen flow rate of 5.5 sccm controlled by a 0–20 sccm range mass flow controller with a readout. The argon–hydrogen gas mixture which produced the maximum VUV emission was determined by adjusting the flow rate of hydrogen and argon with two mass flow controllers such that the total was 5.5 sccm.

The experimental set-up of a type I light source shown in figure 1 comprised a quartz cell which was 500 mm in length and 50 mm in diameter. A Pyrex cap sealed to the quartz cell with a Viton O ring and a C-clamp incorporated ports for gas inlet, outlet and photon detection. A tungsten filament heater (0.508 mm in diameter and 800 cm in length, total resistance ∼2.5 Ω) and hydrogen dissociator were in the quartz tube as well as a cylindrical titanium screen (300 mm long and 40 mm in diameter) that served as a second hydrogen dissociator in the case of the hydrogen gas experiments. A new dissociator was used for each hydrogen gas experiment. The filament
Figure 4. Cylindrical stainless steel gas cell comprising a type IV light source for plasma studies with (1) hydrogen, argon or argon–hydrogen mixture alone, (2) hydrogen with strontium, sodium, magnesium or barium, and (3) argon–hydrogen mixture (77/23%) with strontium.

was coiled on a grooved ceramic tube support to maintain its shape when heated. The return lead passed through the inside of the ceramic tube. The titanium screen was electrically floated. Power was applied to the filament by a dc power supply which was controlled by a constant power controller. The temperature of the tungsten filament was estimated to be in the range 1100–1500 °C. The external cell wall temperature was about 700 °C. The entire quartz cell was enclosed in an alumina insulation package. Several K-type thermocouples were located in the insulation. The thermocouples were monitored with a multichannel computer data acquisition system.

In the present study, the light emission phenomena was studied for
(1) hydrogen, argon, neon and helium alone;
(2) sodium, magnesium, barium and strontium metals alone;
(3) sodium, magnesium, barium and strontium with hydrogen; and
(4) sodium, magnesium, barium and strontium with an argon–hydrogen mixture (97/3%).

1 g of the pure metal (Alfa Aesar 99.95%) of sodium, magnesium, barium or strontium was placed in the centre of the cell under one atmosphere of dry argon in a glovebox. The cell was sealed, removed from the glovebox and connected to a VUV spectrometer. Each metal was vapourized by the filament heater. The power applied to the filament was 300 W in the case of strontium and up to 600 W in the case of magnesium, barium or sodium metal. The voltage across the filament was about 55 V and the current was about 5.5 A at 300 W. For each control, sodium, magnesium or barium metal, the cell temperature was increased to the maximum permissible with the power supply.
The light emission was introduced to a VUV spectrometer for spectral measurement. The spectrometer was a 0.2 m monochromator (Seya-Namioka mounting) equipped with a 1200 line/mm holographic grating with a platinum coating. The wavelength region covered by the monochromator was 30–560 nm. A channel electron multiplier (CEM) was used to detect the VUV light. The wavelength resolution was about 0.2 nm (FWHM) with an entrance and exit slit width of 40 µm. The vacuum inside the monochromator was maintained below $5 \times 10^{-4}$ Torr by a turbo pump. The VUV spectrum (40–160 nm) of the cell emission with strontium present was recorded at about the point of the maximum Lyman $\alpha$ emission.

The UV/VIS spectrum (40–560 nm) of the cell emission with hydrogen alone was recorded with a photomultiplier tube (PMT) and a sodium salicylate scintillator. The PMT used had a spectral response in the range of 185–680 nm with a peak efficiency at about 400 nm. The scan interval was 0.2 nm. The inlet and outlet slit were 40 µm with a corresponding wavelength resolution of 0.2 nm.

Standard VUV emission spectra of hydrogen and argon were obtained with a type II light source comprising a microwave plasma system and a VUV spectrometer shown in figure 2. The microwave generator was a Opthos model MPG-4M generator (frequency: 2450 MHz). The input power to the plasma was set at about 85 W. Hydrogen or argon was flowed through a quartz tube (1.25 cm ID, 20 cm long) at 500 mTorr. The tube was fitted with an Opthos coaxial microwave cavity (Evenson cavity) and was directly connected to the collimator port of a VUV spectrometer. In the case of hydrogen, the VUV spectrometer was the McPherson model 302 normal incidence monochromator. The monochromator slits were 100 µm × 100 µm. A sodium salicylate converter was used and the emission was detected with a PMT detector (Hamamatsu R1527P). To achieve higher sensitivity at the shorter VUV wavelengths, the argon plasma light emission was recorded with a McPherson 4° grazing incidence VUV spectrometer (Model 248/310G) equipped with a grating having 600 G mm$^{-1}$ with a radius of curvature of $\approx$1 m. The angle of incidence was 87°. The wavelength region covered by the monochromator was 1–65 nm. The wavelength resolution was about 0.1 nm (FWHM) with an entrance and exit slit width of 50 µm. A CEM was used to detect the VUV light. The vacuum inside the monochromator was maintained below $5 \times 10^{-4}$ Torr by a turbo pump.

2.2. Balmer line broadening recorded by high resolution visible spectroscopy on rt plasmas

The method of Videnovic et al [9] was used to calculate the energetic hydrogen atom densities and energies from the intensities and width of the 656.3 nm Balmer $\alpha$ line emitted from glow discharge and microwave plasmas. The full half-width $\Delta \lambda_G$ of each Gaussian results from the Doppler ($\Delta \lambda_D$) and instrumental ($\Delta \lambda_I$) half-widths:

$$\Delta \lambda_G = \sqrt{\Delta \lambda_D^2 + \Delta \lambda_I^2}.$$  (1)

$\Delta \lambda_I$ in our experiments was 0.025 nm or ±0.006 nm. The temperature was calculated from the Doppler half-width using the formula

$$\Delta \lambda_D = 7.16 \times 10^{-7} \lambda_0 \left( \frac{T}{\mu} \right)^{1/2} \text{(nm)}$$  (2)

where $\lambda_0$ is the line wavelength in nm, $T$ is the temperature in K (1 eV = 11 605 K) and $\mu$ is the atomic weight (=1 for hydrogen). In each case, the average Doppler half-width that was not appreciably changed with pressure varied by a corresponding error in the energy of ±4%. The

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corresponding number densities for noble gas–hydrogen mixtures varied by ±8%, depending on the pressure.

The width of the 656.3 nm Balmer \( \alpha \) line was recorded on light emitted from a hydrogen glow discharge performed according to methods reported previously [23] and maintained in the cylindrical stainless steel gas cell comprising a type III light source shown in figure 3 that served as a control for measurements recorded of light emitted from rt plasmas of hydrogen with strontium or strontium with an argon–hydrogen mixture (97/3%) maintained in type I cells. The inorganic test materials were coated on a titanium screen dissociator by the method of wet impregnation. The screen was coated by dipping it in a 0.6 M \( \text{SrCO}_3/10\% \), \( \text{H}_2\text{O}_2 \) and the crystalline material was dried on the surface by heating for 12 h in a drying oven at 130°C.

The plasma emission from the hydrogen glow discharge (type III light source) and each rt plasma maintained in the filament heated cell (type I light source) was fibre-optically coupled through a 220F matching fibre adapter positioned 2 cm from the sapphire window or cell wall, respectively, to a high resolution visible spectrometer with a resolution of ±0.006 nm over the spectral range 190–860 nm. The spectrometer was a Jobin Yvon Horiba 1250 M with 2400 groove/mm ion-etched holographic diffraction grating. The entrance and exit slits were set to 20 \( \mu \)m. The spectrometer was scanned between 655.5 and 657 nm using a 0.01 nm step size. The signal was recorded by a PMT with a stand-alone high voltage power supply (950 V) and an acquisition controller. The data was obtained in a single accumulation with a 1 s integration time. The high resolution visible spectrum at 400–410 nm was also recorded in the strontium plasma to record \( \text{Sr} \) and \( \text{Sr}^+ \) lines.

In addition, the width of the 656.3 nm Balmer \( \alpha \) line emitted from gas discharge plasmas having atomized hydrogen from pure hydrogen alone, hydrogen with magnesium or strontium, a mixture of 10% hydrogen and helium, argon, krypton or xenon, a mixture of 10% hydrogen and helium or argon with strontium, and argon with strontium was measured with a high resolution visible spectrometer with a resolution of ±0.025 nm over the spectral range 190–860 nm. The plasmas were maintained in a type III light source.

The 304-stainless steel cylindrical cell was 9.21 cm in diameter and 14.5 cm in height. The base of the cell contained a welded-in stainless steel thermocouple well (1 cm OD) which housed a thermocouple probe in the cell interior approximately 2 cm from the discharge and 2 cm from the cell axis. At the middle height of the cell wall was a welded-flush stainless steel tube (0.95 cm diameter) which was connected to a flexible stainless steel tube (100 cm in length) that served as a vacuum line from the cell and the line to supply the test gas. The top end of the cell was welded to a high vacuum 11.75 cm diameter conflat flange. A silver plated copper gasket was placed between a mating flange and the cell flange. The two flanges were clamped together with 10 circumferential bolts. The mating flange contained two penetrations comprising

1. a stainless steel thermocouple well (1 cm OD) also housing a thermocouple probe in the cell interior approximately 2 cm from the discharge and 2 cm from the cell axis, and
2. a centred high voltage feedthrough which transmitted the power, supplied through a power connector, to a hollow cathode inside the cell.

The axial hollow cathode glow discharge electrode assembly comprised a stainless steel plate (42 mm diameter, 0.9 mm thick) anode and a circumferential stainless steel cylindrical frame (5.08 cm OD, 7.2 cm long) perforated with evenly spaced 1 cm diameter holes. The cathode was attached to the cell body by a stainless steel wire and the cell body was grounded.
A 1.6 mm thick UV-grade sapphire window with 1.5 cm view diameter provided a visible light path from inside the cell. The viewing direction was normal to the cell axis.

Strontium (99.9%) or magnesium (99.98%) metal was coated onto the cathode in a glove box under a dry argon atmosphere. The cell was sealed in the glove box, removed and then evacuated with a turbo vacuum pump to a pressure of 4 mTorr. The gas was ultrahigh purity hydrogen or noble gas–hydrogen mixture (90/10%) at 2 Torr total pressure. The pressure of each test gas comprising a mixture with 10% hydrogen was determined by adding the pure noble gas to a given pressure and increasing the pressure with hydrogen gas to a final pressure. The partial pressure of the hydrogen gas was given by the incremental increase in total gas pressure monitored by a 0–10 Torr absolute pressure gauge. The discharge was carried out under static gas conditions. The discharge was started and maintained by a dc electric field supplied by a constant voltage dc power supply at 275 V which produced a current of about 0.2 A. In the case of strontium–hydrogen and argon–hydrogen plasmas, the voltage was increased at 50 V increments from 275 to 475 V and the high resolution visible spectra were recorded to observe the effect of voltage on the Balmer $\alpha$ line broadening.

The plasma emission from the glow discharges of pure hydrogen and noble gas–hydrogen mixtures was fibre-optically coupled to the spectrometer through a 220F matching fibre adapter. The entrance and exit slits were set to 20 $\mu$m. The spectrometer was scanned between 656 and 657 nm using a 0.01 nm step size. The signal was recorded by a PMT with a stand-alone high voltage power supply (950 V) and an acquisition controller. The data was obtained in a single accumulation with a 1 s integration time.

The electron density and temperature of the rt plasma was determined using a compensated Langmuir probe according to the method given previously [24].

2.3. Power cell apparatus and procedure

Optical power balances were measured on discharge plasmas with

1. hydrogen, argon or argon–hydrogen mixture alone,
2. hydrogen with strontium, sodium, magnesium or barium, and
3. argon–hydrogen mixture (77/23%) with strontium.

The studies were carried out in the cylindrical stainless steel gas cell comprising a type IV light source shown in figure 4 that was heated in a 10 kW refractory brick kiln. The cell was evacuated and pressurized with hydrogen, argon, or argon and hydrogen through a single 0.95 cm feedthrough. The discharge was started and maintained by an alternating current electric field in the 1.75 cm annular gap between an axial electrode and the cell wall. The cylindrical cell was 9.21 cm in diameter and 14.5 cm in height. The axial electrode was a 5.08 cm OD by 7.2 cm long stainless steel tube wound with several layers of nickel screen. The overall diameter of the axial electrode was 5.72 cm. Optical access to the cell was as described in section 2.2 except that an 8 mm quartz rod channelled the light from the view port through a stainless steel tube to a collimating lens which was focused on a 100 $\mu$m optical fibre located outside the furnace. Spectral data was recorded with a visible spectrometer and stored in a personal computer.

The field voltage was controlled by a variable voltage transformer operating from 115 VAC, 60 Hz. A step-up transformer was used when necessary. True rms voltage at the axial electrode was monitored by a digital multimeter. A second multimeter in series with the discharge gap was used to indicate the current. The cell temperature was measured by thermocouple probes.
located in the cell interior as described in section 2.2. Pressure in the hydrogen and argon supply tube outside the furnace was monitored by 10 and 1000 Torr absolute pressure gauges. In the absence of gas flow, the gas supply tube pressure was essentially the cell pressure. The pressure of each gas in an argon–hydrogen mixture was determined by adding one pure gas to a given pressure and increasing the pressure with a second gas to a final pressure. The partial pressure of the second gas was given by the incremental increase in total gas pressure.

Strontium (99.9%), sodium (99.95%), magnesium (99.98%) or barium (99.99%) metal was loaded into the cell under a dry argon atmosphere. The cell was evacuated with a turbo vacuum pump to a pressure of 4 mTorr during most of the heating process. During the heat-up the cell was periodically pressurized with hydrogen (99.999% purity) to approximately 100 Torr and subsequently evacuated to purge gaseous contaminants from the system. When the cell temperature stabilized, hydrogen was added until the steady pressure was approximately 1 Torr. The field voltage was increased until breakdown occurred. This was confirmed by the spectrometer response to visible light emitted from the cell. The hydrogen or hydrogen–argon pressure was adjusted, as much as possible, to maximize the light emission from the cell. The voltage was maintained at the minimum level which resulted in a stable discharge during data acquisition.

The spectrometer system comprised a 100 µm optical fibre and visible spectrometer. To correct for the nonuniform response of the spectrometer system as a function of wavelength and the dependence of energy on wavelength, the system was calibrated against a reference light source. A spectral calibration factor was applied to the count rate data at each wavelength to yield the irradiation of the detector in units of energy/time/area/wavelength. The total visible radiant flux incident on the detector was calculated by integrating the spectral irradiation between 400 and 700 nm.

### 3. Results

#### 3.1. VUV spectroscopy

The cell was operated without any test material present to establish the baseline of the spectrometer. No emission was observed except for the low level blackbody filament radiation at the longer wavelengths. The intensity of the Lyman α emission as a function of time and the VUV/UV/VIS spectra (40–560 nm) was observed at 700 °C from the gas cell comprising a tungsten filament, a titanium dissociator and (1) hydrogen, argon, neon or helium alone, (2) sodium, magnesium or barium metal, or (3) sodium, magnesium or barium metal with 300 mTorr hydrogen with a flow rate of 5.5 sccm. No emission was observed in any case. The maximum filament power was greater than 500 W. A metal coating formed in the cap of the cell over the course of the experiment in each case with a metal vapourized by filament heating.

The intensity of the Lyman α emission as a function of time from the gas cell at a cell temperature of 700 °C comprising a tungsten filament, a titanium dissociator, vapourized strontium metal and 300 mTorr hydrogen at a flow rate of 5.5 sccm is shown in figure 5. Strong emission was observed from vapourized strontium and hydrogen. The VUV spectrum (90–130 nm) of the cell emission recorded at about the point of maximum Lyman α emission is shown in figure 6. No emission was observed in the absence of hydrogen flow. A metal coating formed in the cap of the cell over the course of the experiment.

Hydrogen was replaced by a 97% argon and 3% hydrogen mixture at a total flow rate of 5.5 sccm. The intensity of the Lyman α emission as a function of time and the VUV spectra (40–
Figure 5. The intensity of the Lyman $\alpha$ emission as a function of time from the type I light source. The gas cell at a cell temperature of 700 °C comprised a tungsten filament, a titanium dissociator, vapourized strontium metal and 300 mTorr hydrogen that was recorded with a CEM.

160 nm) at 700 °C was observed for the gas cell comprising a tungsten filament and (1) 300 mTorr argon–hydrogen mixture (97/3%) and (2) vapourized sodium, magnesium or barium metal with 300 mTorr argon–hydrogen mixture (97/3%). No emission was observed in any case.

The VUV spectrum (80–130 nm) of the cell emission recorded at about the point of maximum Lyman $\alpha$ emission from the gas cell at a cell temperature of 700 °C comprising a tungsten filament, vapourized strontium metal and 300 mTorr argon–hydrogen mixture (97/3%) is shown in figure 7. Strong VUV emission was observed that was more intense than with hydrogen and strontium. The Lyman series corresponding to atomic hydrogen emission and strong Ar II ion emission was observed at 92.0 and 93.2 nm.

The rt plasma required the presence of hydrogen. The zero-order emission in the VUV was observed with titration of increasing partial pressure of hydrogen added to argon gas. It was found that increasing the hydrogen pressure initially increased the atomic hydrogen emission lines, but with increasing hydrogen partial pressure at a constant total pressure the Ar II emission in the VUV at 92.0 and 93.2 nm decreased, which resulted in a decrease of the plasma intensity including the hydrogen emission. The optimum argon–hydrogen gas mixture which produced the greatest emission was determined to be 95% argon and 5% hydrogen, which is similar to the 97% argon and 3% hydrogen mixture of Grimm-type discharges studied by Kuraica and Konjevic [8] and Videnovic et al [9]. The optimum ratio was consistent with an rt discharge mechanism which required maximum concentrations of both atomic hydrogen and Ar$^+$. 

3.2. VUV emission of Sr$^+$ catalyst and Ar$^+$ catalyst formed with strontium

The second and third ionization energies of strontium are 11.030 13 and 42.89 eV, respectively [22]. The ionization reaction of Sr$^+$ to Sr$^{3+}$, then, has a net enthalpy of reaction of
The VUV spectrum (90–130 nm) of the type I light source emission recorded at about the point of the maximum Lyman $\alpha$ emission. The gas cell at a cell temperature of 700 °C comprised a tungsten filament, a titanium dissociator, vapourized strontium metal and 300 mTorr hydrogen that was recorded with a CEM.

53.92 eV, which is about $2 \times 27.2$ eV; thus, Sr$^+$ may serve as a catalyst to form an rt plasma. The VUV spectrum (35–67 nm) of the emission of a strontium rt plasma type I light source is shown in figure 8. Line emission corresponding to Sr$^{3+}$ that confirmed the catalyst mechanism was observed at 66.4, 41.35 and 39.6 nm, which matched NIST tables [25]. Sr$^{2+}$ was observed at 56.3, 51.4, 49.2 and 43.7 nm. The presence of the Sr$^+$ catalyst was confirmed by the Sr$^+$ line emission shown in figure 9 at 407.77 nm, which matched NIST tables [25].

The VUV spectra (30–170 nm) and (24–41 nm) regions of the emission of a strontium–argon–hydrogen rt plasma type I light source are shown in figures 10 and 11, respectively. The VUV spectra (20–62.5 nm) and (38–50 nm) of control hydrogen and argon microwave plasma type II light sources are shown in figures 12 and 13, respectively. In addition to Ar$^+$ and Ar$^{2+}$ emission, a broad continuum emission band in the region of 45.6 nm (27.2 eV) was observed in the strontium–argon–hydrogen gas cell emission that was not present in the control hydrogen or argon control plasmas. Rather, the entire Rydberg series of lines of Ar$^+$ is observed in the argon control with a discontinuity of the series at the limit of the ionization energy of Ar$^+$ to Ar$^{2+}$ at 44.9 nm.

3.3. Line broadening measurements type I cells

The results of the 656.3 nm Balmer $\alpha$ linewidth measured with a high resolution ($\pm 0.006$ nm) visible spectrometer on light emitted from rt plasmas of hydrogen with SrCO$_3$ and SrCO$_3$ with an argon–hydrogen mixture (97/3%) maintained in type I cells are shown in figures 14 and 15, respectively. The Balmer $\alpha$ linewidth and energetic hydrogen atom densities and energies given in table 1 were calculated using the method of Videnovic et al [9]. Significant line

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Figure 7. The VUV spectrum (80–130 nm) of the type I light source emission recorded at about the point of the maximum Lyman $\alpha$ emission. The gas cell at a cell temperature of 700 °C comprised a tungsten filament, vapourized strontium metal and 300 mTorr argon–hydrogen mixture (97/3%) that was recorded with a PMT and a sodium salicylate scintillator.

broadening of 14 and 24 eV and atom densities of $8 \times 10^{11}$ and $4 \times 10^{11}$ atoms cm$^{-3}$ were observed from an rt plasma of hydrogen formed with strontium, and strontium with Ar$^+$ catalysts, respectively. A glow discharge of hydrogen maintained at the same total pressure showed no excessive broadening corresponding to an average hydrogen atom temperature of $\approx 3$ eV. The superposition of the 656.3 nm Balmer $\alpha$ linewidth recorded with a high resolution ($\pm 0.006$ nm) visible spectrometer on a hydrogen–strontium rt plasma and a hydrogen–strontium rt plasma intensified by an argon ion catalyst is shown in figure 16. By comparison to the strontium rt plasma, significant broadening attributable to an argon ion was observed corresponding to an average hydrogen atom temperature of 24 versus 14 eV. The atom density was also very high in the argon rt plasma, given that the hydrogen concentration was 30 times less than that of the strontium–pure hydrogen rt plasma.

3.4. Line broadening measurements on type III cells

The 656.3 nm Balmer $\alpha$ linewidth was measured on type III light sources normal to the applied electric field direction with a high resolution ($\pm 0.025$ nm) visible spectrometer. The discharge was started and maintained at 2 Torr total pressure by a dc electric field supplied by a constant voltage dc power supply at 275 V, which produced a current of about 0.2 A. The results of the gas discharge plasmas of a mixture of 10% hydrogen and 90% xenon, strontium with hydrogen and 10% hydrogen with helium or argon and strontium, each compared to control hydrogen alone, are given in figures 17–20, respectively. In addition, the emission of a strontium–argon plasma in the region of the Balmer $\alpha$ line was recorded, as shown in figure 20. Sr I emission was observed at 655 nm, but no emission was observed in the region of the Balmer $\alpha$ line, which eliminated the
The VUV spectrum (35–67 nm) of a strontium rt plasma type I light source emission. Line emission corresponding to Sr\(^{3+}\) that confirmed the catalyst mechanism was observed at 66.4, 41.35 and 39.6 nm. Sr\(^{2+}\) was observed at 56.3, 51.4, 49.2 and 43.7 nm.

Possibility that a strontium line close to the Balmer \(\alpha\) line was the source of the line broadening with strontium present. The Balmer \(\alpha\) linewidth and energetic hydrogen atom densities and energies are given in table 1. It was found that strontium–hydrogen, helium–hydrogen, argon–hydrogen, strontium–helium–hydrogen and strontium–argon–hydrogen plasmas showed significant broadening corresponding to an average hydrogen atom temperature of 23–45 eV, whereas pure hydrogen, krypton–hydrogen, xenon–hydrogen and magnesium–hydrogen showed no excessive broadening corresponding to an average hydrogen atom temperature of \(\approx 4\) eV. No voltage effect was observed with the argon–hydrogen and strontium–hydrogen plasmas.

3.5. Optically measured power balance

The count rate and spectrometer system irradiation of the background spectrum of hydrogen and strontium vapour over the wavelength range \(400 \text{ nm} \leq \lambda \leq 700 \text{ nm}\) in the absence of power applied to the electrode and in the absence of a discharge was measured. This data was collected during cell evacuation following the test with strontium and hydrogen at a cell temperature of 664 °C. The maximum visible irradiation of 0.004 \(\mu\)W cm\(^{-2}\) nm\(^{-1}\) occurred at the red end of the visible spectrum. The results are summarized in table 2 where \(T\) is the temperature, \(P_{\text{hyd}}\) and \(P_{\text{Ar}}\) are the hydrogen and argon partial pressures and \(P_v\) is the equilibrium metal vapour pressure calculated from standard curves of the vapour pressure as a function of temperature [27].

Power was applied to the electrode to achieve a bright plasma in the strontium–hydrogen mixture and the controls of hydrogen alone, and sodium–hydrogen, magnesium–hydrogen and barium–hydrogen mixtures for cell temperatures in the range 335–666 °C. In each case, the spectral radiant flux at the spectrometer system was recorded. If possible, the power driving the controls was adjusted such that the peak spectrometer system spectral irradiation was about

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Figure 9. The high resolution visible spectrum (400–410 nm) of a strontium rt plasma type I light source emission. Line emission corresponding to Sr$^+$ was observed at 407.77 nm. Sr was observed at 403.03 nm.

0.1 $\mu$W cm$^{-2}$ nm$^{-1}$ in each case. The integrated visible irradiation levels were of the order of 1 $\mu$W cm$^{-2}$. One exception was the case of hydrogen–barium. In this case, the maximum spectral irradiation levels and integrated visible irradiation levels were only of the order of 0.01 $\mu$W cm$^{-2}$ nm$^{-1}$ and 0.03 $\mu$W cm$^{-2}$, respectively.

The power required to maintain a plasma of equivalent optical brightness with strontium atoms present was 4000, 7000 and 6500 times less than that required for the sodium, magnesium and barium control, respectively. A driving power of 33.7 and 58 W was necessary to achieve a total visible radiant flux of about 1 $\mu$W cm$^{-2}$ from a sodium–hydrogen mixture and a magnesium–hydrogen mixture, respectively. For a hydrogen–barium mixture, a power input of about 55 W was required to achieve a total visible irradiation of about 0.03 $\mu$W cm$^{-2}$, whereas, in the case of a strontium–hydrogen mixture, a power input of 8.5 mW resulted in a plasma with a total visible radiant flux of about the same optical brightness as sodium and magnesium. A plasma formed at a cell voltage of about 250 V for hydrogen alone and sodium–hydrogen mixtures, and 140–150 V for hydrogen–magnesium and hydrogen–barium mixtures, whereas a plasma formed for hydrogen–strontium mixtures at the extremely low voltage of about 2 V. The results are summarized in table 2.

Power was applied to the electrode to achieve a bright plasma in the strontium–argon–hydrogen mixture and the controls of argon alone and argon–hydrogen alone for cell temperatures in the range 514–520 °C. In each case, the spectral radiant flux at the spectrometer system was recorded. If possible, the power driving the controls was adjusted such that the peak spectrometer system spectral irradiation was about 0.1 $\mu$W cm$^{-2}$ nm$^{-1}$ in each case. The integrated visible irradiation levels were of the order of 1 $\mu$W cm$^{-2}$.

The power required to maintain a plasma of equivalent optical brightness with strontium atoms present was 8600 and 6300 times less than that required for argon–hydrogen and argon
Figure 10. The VUV spectrum (30–170 nm) of the cell emission from a type I light source comprising a gas cell at a cell temperature of 700 °C with a tungsten filament, vapourized strontium metal and 300 mTorr argon–hydrogen mixture (97/3%) that showed Ar⁺, Ar²⁺ and 27.2 eV emission, which supported a resonant-energy-transfer mechanism of 27.2 eV from atomic hydrogen to Ar⁺ to form Ar²⁺.

Figure 11. The VUV spectrum (24–41 nm) of the cell emission from a type I light source comprising a gas cell at a cell temperature of 700 °C with a tungsten filament, vapourized strontium metal and 300 mTorr argon–hydrogen mixture (97/3%) that showed Ar²⁺ emission, which supported a resonant-energy-transfer mechanism.

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Figure 12. Standard VUV hydrogen emission spectrum (20–62.5 nm) recorded on a type II light source with a McPherson model 302 VUV spectrometer, a PMT and a sodium salicylate scintillator.

control, respectively. A driving power of 33.5 and 24.7 W was necessary to achieve a total visible radiant flux of about 1 $\mu$W cm$^{-2}$ from an argon–hydrogen mixture and argon, respectively, whereas, in the case of a strontium–argon–hydrogen mixture, a power input of 4 mW resulted in a plasma with a total visible radiant flux of about the same optical brightness as the argon–hydrogen mixture and argon alone. A plasma formed at a cell voltage of 224 V for an argon–hydrogen mixture and 190 V for argon alone, whereas a plasma formed for argon–hydrogen–strontium mixtures at an extremely low voltage of about 6.6 V. The results are summarized in table 2.

4. Discussion

Intense VUV emission was observed at low temperatures (e.g. $\approx 10^3$ K) from atomic hydrogen and strontium which ionizes at an integer multiple of the potential energy of atomic hydrogen. The emission intensity of the rt plasma generated by strontium increased significantly with the introduction of argon gas only when Ar$^+$ emission was observed. The ionization energy of Ar$^+$ to Ar$^{2+}$ is 27.6 eV. In the cases where Lyman $\alpha$ emission was observed, no possible chemical reactions of the tungsten filament, the dissociator, the vapourized strontium and 300 mTorr hydrogen or argon–hydrogen mixture at a cell temperature of 700 $^\circ$C could be found which accounted for the hydrogen $\alpha$ line emission. In fact, no known chemical reaction releases enough energy to excite Lyman $\alpha$ emission from hydrogen. The emission was not observed with hydrogen or an argon–hydrogen mixture alone or with helium, neon or argon gas. Intense emission was observed for strontium with hydrogen gas, but no emission was observed with hydrogen or strontium alone. This result indicates that the emission may be due to a reaction of hydrogen. The increase in intensity with the formation of Ar$^+$ and the equal dependence of the
emission on the presence of both $\text{Ar}^+$ and atomic hydrogen indicates a reaction between these species. A similar effect reported previously [15] was also observed when helium was added to a hydrogen plasma which depended on the presence of $\text{He}^+$ and atomic hydrogen.

The characteristic emission from Sr$^+$ and Sr$^{3+}$ confirmed the resonant nonradiative energy transfer of $2 \times 27.2$ eV from atomic hydrogen to Sr$^+$. Atomic strontium may serve as a catalyst as well which may initiate the rt plasma and form Sr$^+$ [15]. With a highly conductive plasma, the voltage of the cell was about 20 V and the field strength was about 1–2 V cm$^{-1}$, which was too low to ionize Sr$^+$ to Sr$^{3+}$, which requires at least 53.92 eV; rather, a resonant energy transfer explains the observations.

The balanced catalytic reaction of argon was given previously [14]. Characteristic emission was also observed from a continuum state of Ar$^{2+}$ which confirmed the resonant nonradiative energy transfer of 27.2 eV from atomic hydrogen to Ar$^+$. In the rt plasma due to the presence of Ar$^+$, atomic hydrogen may resonantly transfer energy to Ar$^+$ to cause its ionization to Ar$^{2+}$ which may then decay and emit the radiation. The vacuum reaction in the absence of an electric field is

$$\text{Ar}^{2+} + e^- \rightarrow \text{Ar}^+ + 27.63 \text{ eV}.$$  

In the catalysis of atomic hydrogen by Ar$^+$, a weak electric field may adjust the energy of ionizing Ar$^+$ to Ar$^{2+}$ to match the energy of 27.2 eV to permit the catalysis. The transfer of 27.2 eV from atomic hydrogen to Ar$^+$ in the presence of the weak field of the filament results in its excitation to a continuum state. Then the energy for the transition from essentially the Ar$^{2+}$ state to the lowest state of Ar$^+$ is predicted to give a broad continuum radiation in the region of 45.6 nm. This broad continuum emission was observed. This emission was different from that given by an argon microwave plasma wherein the entire Rydberg series of lines of Ar$^+$ was observed with a discontinuity of the series at the limit of the ionization energy of Ar$^+$ to Ar$^{2+}$. The observed
Line broadening of the hydrogen Balmer lines provides a sensitive measure of the number and energy of excited hydrogen atoms in a plasma. To further characterize the plasma parameters of rt plasmas, the width of the 656.3 nm Balmer line was recorded on light emitted from rt plasmas formed from hydrogen with a gaseous ion which ionizes at integer multiples of the potential energy of atomic hydrogen. The energetic hydrogen atom densities and energies were determined from the intensities and broadening, and it was found that significant line broadening of 14 and 24 eV and an atom density of $8 \times 10^{11}$ and $4 \times 10^{11}$ atom cm$^{-3}$ were observed from an rt plasma of hydrogen formed with strontium, and strontium with Ar$^+$ catalysts, respectively, whereas a glow discharge of hydrogen maintained at the same total pressure with an electric field strength that was at least two orders of magnitude greater than the 1 V cm$^{-1}$ field of the filament cell showed no excessive broadening corresponding to an average hydrogen atom temperature of $\approx 3$ eV.

In the characterization of argon–hydrogen (97/3%) Grimm-type plasma discharges with a hollow anode, Kuraica and Konjevic [8] and Videnovic et al [9] analysed the broadening data in terms of Stark and Doppler effects wherein acceleration of charges such as H$^+$, H$_2^+$ and H$_3^+$ in the high fields (e.g. over 10 kV cm$^{-1}$) which were present in the cathode fall region was used to explain the Doppler component. In our experiments with type I cells, the measured field of the incandescent heater was extremely weak, 1 V cm$^{-1}$, corresponding to a broadening much less than 1 eV. Thus we have assumed that Doppler broadening due to thermal motion was the dominant source in the rt plasmas, to the extent that other sources may be neglected. In general, the experimental profile is a convolution of a Doppler profile, an instrumental profile,
Figure 15. The 656.3 nm Balmer $\alpha$ linewidth recorded with a high resolution ($\pm 0.006$ nm) visible spectrometer on the type I light source emission of a hydrogen–strontium rt plasma intensified by an argon ion catalyst. Significant broadening was observed corresponding to an average hydrogen atom temperature of 24 eV.

Figure 16. The superposition of the 656.3 nm Balmer $\alpha$ linewidth spectra recorded on the type I light source emission of a hydrogen–strontium rt plasma and a hydrogen–strontium rt plasma intensified by an argon ion catalyst. By comparison to the strontium rt plasma, significant broadening attributable to argon ions was observed, corresponding to an average hydrogen atom temperature of 24 eV versus 14 eV.

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the natural (lifetime) profile, Stark profiles, van der Waals profiles, a resonance profile and fine structure. The source of broadening was confirmed to be Doppler alone by considering each possible source according to the methods described previously [28, 29]. For example, using a compensated Langmuir probe [24], the electron density was measured to be $n_e < 10^{10}$ cm$^{-3}$, which is at least five orders of magnitude too low to invoke Stark broadening, as discussed previously [28, 29].

It was reported previously [28, 29] that microwave helium–hydrogen and argon–hydrogen plasmas showed extraordinary broadening corresponding to an average hydrogen atom temperature of 180–210 eV and 110–130 eV, respectively, whereas pure hydrogen and xenon–hydrogen microwave plasmas showed no excessive broadening corresponding to an average hydrogen atom temperature of $\approx 4$ eV. No hydrogen species (H$^+$, H$_2^+$, H$_3^+$, H$^-$, H or H$_2$) responds to the microwave field; rather, only the electrons respond. But the measured electron temperature was about 1 eV which requires that $T_H \gg T_e$. This result cannot be explained by electron or external Stark broadening or electric field acceleration of charged species. The electron density was five orders of magnitude too low [28, 29] for detectable Stark broadening. And, in microwave driven plasmas, there is no high electric field in a cathode fall region ($> 1$ kV cm$^{-1}$) to accelerate positive ions as proposed previously [9, 30]–[32] to explain significant broadening in hydrogen containing plasmas driven at high voltage electrodes. It is impossible for H, or any H-containing ion which may give rise to H, to have a higher temperature than the electrons in a microwave plasma. The observation of excessive Balmer line broadening in a microwave driven plasma requires a source of energy other than that provided by the electric field. All conventional explanations were exhausted [33]. The formation of fast H was explained by a resonant energy transfer between hydrogen atoms and Ar$^+$ or He$^+$ of an integer multiple of the potential energy of atomic hydrogen, 27.2 eV. Similarly, the source of the excessive line broadening in the strontium and argon–strontium rt plasmas is consistent with that of VUV emission, an energetic reaction

### Table 1. Energetic hydrogen atom densities and energies for rt plasmas and ordinary hydrogen plasmas maintained in type I and type III light sources.

| Plasma gas | Light source type | Hydrogen atom density$^a$ ($10^{12}$ atom cm$^{-3}$) | Hydrogen atom energy$^b$ (eV) |
|------------|-------------------|---------------------------------|-------------------------------|
| H$_2$      | III               | 50                              | 3–5                           |
| Mg/H$_2$   | III               | 60                              | 4–5                           |
| Kr/H$_2$   | III               | 10                              | 2.5–3.5                       |
| Xe/H$_2$   | III               | 10                              | 3–4                           |
| Sr/H$_2$   | III               | 100                             | 23–25                         |
| Ar/H$_2$   | III               | 30                              | 30–35                         |
| He/H$_2$   | III               | 30                              | 33–38                         |
| Sr/Ar/H$_2$| III               | 40                              | 35–40                         |
| Sr/He/H$_2$| III               | 40                              | 40–45                         |
| Sr/H$_2$   | I                 | 0.8                             | 14                            |
| Sr/Ar/H$_2$| I                 | 0.4                             | 24                            |

$^a$ Calculated after [9], equations (1)–(2).  
$^b$ Calculated after [9], equations (1)–(2).
Figure 17. The 656.3 nm Balmer $\alpha$ linewidth recorded with a high resolution ($\pm 0.025$ nm) visible spectrometer on a xenon–hydrogen and a hydrogen gas discharge plasma of a type III light source. No excessive line broadening was observed corresponding to an average hydrogen atom temperature of $\approx 3$ eV.

caused by a resonant energy transfer between hydrogen atoms and strontium or Ar$^+$ catalysts. The balanced energetic reactions were given previously [14, 20, 21].

An rt plasma with hydrogen–potassium mixtures has been reported in an experiment identical to the present VUV experiments [18] with type I cells. In this experiment and the one treated in [17], an rt plasma formed with hydrogen–potassium mixtures wherein the plasma decayed with a 2 s half-life when the electric field was set to zero [17]. This was the thermal decay time of the filament which dissociated molecular hydrogen to atomic hydrogen. This experiment showed that hydrogen line emission was occurring even though the voltage between the heater wires was set to and measured to be zero and indicated that the emission was due to a reaction of potassium atoms with atomic hydrogen. Potassium atoms ionize at an integer multiple of the potential energy of atomic hydrogen, $m \times 27.2$ eV. The enthalpy of ionization of K to K$^{3+}$ has a net enthalpy of reaction of $81.7426$ eV, which is equivalent to $m = 3$. The observation of K$^{3+}$ has been reported previously [13].

An rt plasma of hydrogen and certain alkali ions formed at low temperatures ($<10^3$ K) as recorded via VUV spectroscopy and the hydrogen Balmer and alkali line emissions in the visible range [18]. The observed plasma formed from atomic hydrogen generated at a tungsten filament that heated a titanium dissociator and one of potassium, rubidium, caesium and their carbonates and nitrates. These atoms and ions ionize to provide a net enthalpy of reaction of an integer multiple of the potential energy of atomic hydrogen ($m \times 27.2$ eV, $m = $ integer) to within 0.17 eV and comprise only a single ionization in the case of a potassium or rubidium ion. However, the chemically similar atoms of sodium and sodium and lithium carbonates and nitrates, which do not ionize with these constraints, caused no emission. To test the electrical dependence of the emission, the weak electric field of about 1 V cm$^{-1}$ was set and measured
Figure 18. The 656.3 nm Balmer $\alpha$ linewidth recorded with a high resolution ($\pm 0.025$ nm) visible spectrometer on a strontium–hydrogen and a hydrogen gas discharge plasma of a type III light source. Significant broadening was observed corresponding to an average hydrogen atom temperature of 23–25 eV.

Figure 19. The 656.3 nm Balmer $\alpha$ linewidth recorded with a high resolution ($\pm 0.025$ nm) visible spectrometer on a strontium–helium–hydrogen and a hydrogen gas discharge plasma of a type III light source. Significant broadening was observed corresponding to an average hydrogen atom temperature of 40–45 eV.

to be zero in $<0.5 \times 10^{-6}$ s. An afterglow duration of about one to two seconds was recorded in the case of potassium, rubidium, caesium, $K_2CO_3$, RbNO$_3$ and CsNO$_3$. Hydrogen line or alkali line emission was occurring even though the voltage between the heater wires was set to and measured to be zero. These atoms and ions ionize to provide a net enthalpy of reaction of
Figure 20. The 656.3 nm Balmer α linewidth recorded with a high resolution (±0.025 nm) visible spectrometer on a strontium–argon–hydrogen, strontium–argon and a hydrogen gas discharge plasma of a type III light source. Significant broadening was observed corresponding to an average hydrogen atom temperature of 35–40 eV.

an integer multiple of the potential energy of atomic hydrogen to within less than the thermal energies at ≈10^3 K and comprise only a single ionization in the case of a potassium or rubidium ion. Since the thermal decay time of the filament for dissociation of molecular hydrogen to atomic hydrogen was similar to the rt plasma afterglow duration, the emission was determined to be due to a reaction of atomic hydrogen with each of the atoms or ions that did not require the presence of an electric field to be functional.

The width of the 656.3 nm Balmer α line emitted from gas discharge plasmas having atomized hydrogen from pure hydrogen alone, hydrogen with magnesium or strontium, a mixture of 10% hydrogen and helium, argon, krypton or xenon, and a mixture of 10% hydrogen and helium or argon with strontium was also measured with a high resolution (±0.025 nm) visible spectrometer on light emitted from type III cells. The energetic hydrogen atom density and energies were determined from the intensities and broadening and it was found that strontium–hydrogen, helium–hydrogen, argon–hydrogen, strontium–helium–hydrogen and strontium–argon–hydrogen plasmas showed significant broadening corresponding to an average hydrogen atom temperature of 23–45 eV, whereas pure hydrogen, krypton–hydrogen, xenon–hydrogen and magnesium–hydrogen showed no excessive broadening corresponding to an average hydrogen atom temperature of ≈4 eV. Thus, line broadening was only observed for those atoms and ions which provided a net enthalpy of reaction of a multiple of the potential energy of the hydrogen atom.

In our normal glow discharge studies with argon–hydrogen plasmas, the voltage was increased in 50 V increments from 275 to 475 V, and the high resolution visible spectra were recorded to observe the effect of voltage on the Balmer α line broadening. In contrast to an increase in broadening with voltage predicted by Kuraica and Konjevic [8], no voltage effect was observed. Also, no voltage effect was also observed with the strontium–hydrogen plasma which supports the rt plasma mechanism of the low voltage strontium–hydrogen and strontium–argon–hydrogen plasmas reported in section 3.5.
### Table 2. Type IV light source discharge conditions and comparison of the driving power to achieve a total visible radiant flux of about \(1 \mu\text{W cm}^{-2}\).\n
|                | \(T\) (°C) | \(P_{\text{hyd}}\) (Torr) | \(P_{\text{Ar}}\) (Torr) | \(P_v\) (V) | Voltage (V) | Current (mA) | Integ. time (ms) | Detector irradiation (\(\mu\text{W cm}^{-2}\)) | Power (W) |
|----------------|-------------|-----------------------------|---------------------------|------------|-------------|--------------|------------------|----------------------------------------|-----------|
| Ar + H\(_2\) + Sr | 514         | 0.3                         | 1.0                       | 0.006      | 6.56        | 0.6          | 204             | 1.3                                    | 0.0039    |
| Ar + H\(_2\) | 519         | 0.295                       | 0.5                       | —          | 224         | 184          | 409             | 1.9                                    | 33.5\(^b\) |
| Ar             | 520         | —                           | 1.0                       | —          | 190         | 170          | 307             | 1.1                                    | 24.7\(^b\) |
| H\(_2\) + Sr  | 664         | —                           | —                         | 0.270      | 2.20        | 3.86         | 768             | 1.17                                   | 0.0085    |
| H\(_2\)       | 664         | 1.0                         | —                         | —          | 224         | 110          | 1130            | 2.08                                   | 24.6      |
| H\(_2\) + Na  | 335         | 1.0                         | —                         | 0.051      | 272         | 124          | 122             | 1.85                                   | 33.7      |
| H\(_2\) + Na  | 516         | 1.5                         | —                         | 5.3        | 220         | 68           | 768             | 0.40                                   | 15.0      |
| H\(_2\) + Na  | 664         | 1.5                         | —                         | 63         | 240         | 41           | 768             | 0.41                                   | 9.84      |
| H\(_2\) + Mg  | 449         | 4.0                         | —                         | 0.016      | 153         | 380          | 500             | 1.7                                    | 58        |
| H\(_2\) + Mg  | 582         | 4.2                         | —                         | 0.6        | 233         | 290          | 500             | 0.16                                   | 68        |
| H\(_2\) + Mg  | 654         | 3.0                         | —                         | 2.8        | 250         | 400          | 1000            | 0.18                                   | 100.0     |
| H\(_2\) + Ba  | 666         | 2.0                         | —                         | 0.025      | 138         | 730          | 716             | 0.03                                   | 55\(^b\)  |
| Bkgnd         | 664         | —                           | —                         | 0.270      | 0           | 0            | 768             | 0.20                                   | 0         |

\(^a\) Calculated \([27]\).  
\(^b\) Power input differs from volt-amperes due to non-unity power factor.

Since line broadening is a measure of the atom temperature, and a significant increase was observed for strontium or argon with hydrogen, the power balance of a gas cell having vapourized strontium and atomized hydrogen from pure hydrogen or an argon–hydrogen mixture (77/23%) was measured by integrating the total light output corrected for the spectrometer system response and energy over the visible range. A cylindrical nickel mesh hydrogen dissociator of a gas cell also served as an electrode to produce an essentially uniform radial electric field between the dissociator and the wall of the cylindrical stainless steel gas cell. Power was applied to the electrode to achieve a bright plasma which was recorded over the wavelength range \(400 \text{ nm} \leq \lambda \leq 700 \text{ nm}\). Control experiments were identical except that sodium, magnesium or barium replaced strontium. In the case of hydrogen–sodium, hydrogen–magnesium and hydrogen–barium mixtures, 4000, 7000 and 6500 times the power of the hydrogen–strontium mixture was required, respectively, in order to achieve the same optically measured light output power.

With the addition of argon to the hydrogen–strontium plasma, the power required to achieve that same optically measured light output power was reduced by a factor of about two. In the case of an argon–hydrogen mixture and argon alone, the power requirement was 8600 and 6300 times the power input of the argon–hydrogen–strontium mixture, respectively. A plasma formed at a cell voltage of about 250 V for hydrogen alone and sodium–hydrogen mixtures, 140–150 V for hydrogen–magnesium and hydrogen–barium mixtures, 224 V for an argon–hydrogen mixture alone, and 190 V for argon alone, whereas a plasma formed for hydrogen–strontium mixtures and argon–hydrogen–strontium mixtures at extremely low voltages of about 2 and 6.6 V, respectively. This is a two orders of magnitude lower than the starting voltages measured for gas glow discharges \([34, 35]\).
It is well known that a typical dc glow discharge has a cathode fall region corresponding to a sheath where the voltage drops very sharply, giving rise to electric fields of the order of $10 \text{ kV cm}^{-1}$ [9]. These fields accelerate positive ions that strike the cathode to cause ejection of electrons which maintain the plasma discharge. The low voltage of $2–6.6 \text{ V}$ measured between the cathode and anode of the rt plasma in the type IV light source suggests that the typical cathode sheath has a very low voltage drop and the measured voltage actually corresponds to that typical of the plasma region comprising a positive column and the anode sheath. This model of the type IV light source is supported by the formation of a plasma with no field present, rather only heating of a catalyst with atomic hydrogen [33]. In the rt plasma case, the source of electrons to maintain the plasma can be explained by the ionization of electrons from the catalyst with the resonant energy transfer and the ionization of the plasma gas by collisions with the observed energetic hydrogen.

5. Conclusion

An rt plasma formed with a low field ($1 \text{ V cm}^{-1}$), at low temperatures (e.g. $\approx 10^3 \text{ K}$), from atomic hydrogen generated at a tungsten filament and strontium which was vapourized by heating the metal. Strong VUV emission was observed that increased with the addition of argon, but not when sodium, magnesium or barium replaced strontium or with hydrogen, argon or strontium alone. $\text{Ar}^+$, $\text{Ar}^{2+}$ and $27.2 \text{ eV}$ emission supported a resonant-energy-transfer mechanism of $27.2 \text{ eV}$ from atomic hydrogen to $\text{Ar}^+$ to form $\text{Ar}^{2+}$. $\text{Sr}^{3+}$ and $\text{Sr}^+$ emission supported a resonant-energy-transfer mechanism of $2 \times 27.2 \text{ eV}$ from atomic hydrogen to $\text{Sr}^+$ to form $\text{Sr}^{3+}$. The energetic reaction of atomic hydrogen was anticipated to form energetic hydrogen atoms and excessively bright light emission per input power with a very low or absent electric field. Significant Balmer $\alpha$ line broadening corresponding to an average hydrogen atom temperature of 14, 24 and $23–45 \text{ eV}$ was observed for strontium and argon–strontium rt plasmas and discharges of strontium–hydrogen, helium–hydrogen, argon–hydrogen, strontium–helium–hydrogen and strontium–argon–hydrogen, respectively, compared to $\approx 3 \text{ eV}$ for pure hydrogen, krypton–hydrogen, xenon–hydrogen and magnesium–hydrogen. To achieve that same optically measured light output power, hydrogen–sodium, hydrogen–magnesium and hydrogen–barium mixtures required 4000, 7000 and 6500 times the power of the hydrogen–strontium mixture, respectively, and the addition of argon increased those ratios by a factor of about two. A glow discharge plasma formed for hydrogen–strontium mixtures at an extremely low voltage of about $2 \text{ V}$, compared to $250 \text{ V}$ for hydrogen alone and sodium–hydrogen mixtures, and $140–150 \text{ V}$ for hydrogen–magnesium and hydrogen–barium mixtures. The low voltages can be explained by the direct ionization of the catalyst by the resonant energy transfer and the secondary ionization of the plasma gas by collisions with energetic hydrogen.

The observation of rt plasmas formed with strontium and argon at 1% of the theoretical or prior known voltage requirement with a light output per unit power input up to 8600 times that of the control standard light source has implications for an advanced light source.

Acknowledgment

Special thanks are due to Jobin Yvon Horiba, Inc, Edison, NJ for use of the high resolution ($\pm 0.025 \text{ nm}$) visible spectrometer, to Takeyoshi Onuma and Ying Lu for recording VUV spectra, and to Bala Dhandapani and Jiliang He for reviewing this manuscript.

New Journal of Physics 4 (2002) 70.1–70.28 (http://www.njp.org/)
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