A vacuum compatible hyperthermal atom generator includes a membrane having two sides, the membrane having the capability of dissolving atoms into the membrane’s bulk. A first housing is furnished in operative association with the first side of the membrane to provide for the exposure of the first side of the membrane to a gas species. A second housing is furnished in operative association with the second side of the membrane to provide a vacuum environment having a pressure of less than 1×10⁻³ Torr on the second side of the membrane. Exciting means excites atoms adsorbed on the second side of the membrane to a non-binding state so that a portion from 0% to 100% of atoms adsorbed on the second side of the membrane are released from the second side of the membrane primarily as an atom beam.
FIG. 5

QMS signal

16 AMU (O)

19 AMU (H₃O)
FIG. 6
FIG. 7

Remove upstream oxygen

Replace upstream oxygen

T = 440°C

Time, min

0 signal, arbitrary units
FIG. 8

Ion Kinetic Energy, eV

N(E), Arbitrary Units

a

b

ESDIE

0
FIG. 9A

Electron acceleration potential

FIG. 9B

AP, IE=0 modes
FIG. 10

O signal, arbitrary units

Time

FIG. 10
FIG. 11
SMALL VACUUM COMPATIBLE HYPERTHERMAL ATOM GENERATOR

This is a divisional of application(s) Ser. No. 08/356,741, filed on Nov. 21, 1994, U.S. Pat. No. 5,654,541 which is a continuation in part of application Ser. No. 08/088,963 filed Jul. 2, 1992, now U.S. Pat. No. 5,367,161, granted Nov. 22, 1994.

ORIGIN OF THE INVENTION

The invention described herein was made jointly by an employee of the United States Government and a nongovernment employee and may be used by or for the Government for governmental purposes without the payment of any royalties thereon or therefor.

BACKGROUND OF THE INVENTION

1. Technical Field of the Invention

This invention relates generally to the dissociation of molecules into atoms, their transport through a solid membrane and their subsequent desorption by electron or photon desorption. In particular, it relates to a device for the production of a high purity, neutral hyperthermal atomic beam generator capable of producing eg. atomic oxygen, nitrogen, hydrogen, and other species, the device being compact and ultrahigh vacuum (UHV), high vacuum, and rough vacuum (<10^-3 Torr) compatible.

2. Description of Related Art

The composition of the atmosphere within the orbital envelope (200–1000 km) combined with the orbital velocity (8 km s^-1) results in a flux of hyperthermal atomic oxygen (E=5 eV×10^13 cm^-2 s^-1) impinging on spacecraft surfaces. The extreme reactivity of atomic oxygen leads to numerous chemical unions with other species to form, for example, CO, CO_2, H_2O, O_2, SO_2, and NO_2. Further, the high chemical reactivity of this O atom flux has caused substantial degradation of organic materials on board the Shuttle and suggests that materials on the proposed Space Station Freedom, the composites used in large space structures, exterior coatings on the optics of the Hubble Space Telescope, the UV telescopes, and future laser communications systems may have substantially reduced lifetimes. It is therefore essential to study the reactivity of these materials to atomic oxygen in ground based laboratories. In order to conduct such laboratory experiments, an atomic oxygen beam generator is required that can accurately simulate the flux and energy (within the appropriate vacuum environment) of the vehicle experience in orbit. In addition to oxygen atom reactions that the vehicle experiences in orbit, and to oxygen atom reactions with spacecraft materials, such a beam system as well as other atomic beam sources would also be of importance in the calibration of mass spectrometers and other detection systems that would be used for mapping the density of gas constituents within the orbital envelope. Such calibration is essential to make accurate measurements of the representative gas environment within the orbital envelope. A pure, well behaved O beam would also be useful for producing an ordered oxide layer for growth of compound semiconductors and superconductors. Methods of thin film growth, such as molecular beam epitaxy (MBE), could fully utilize a directed O atom beam to grow desired layers without the residual contaminating effects of backfield O_2 or the limitations of dissociative adsorption as well as N and H beams for producing high purity nitrides and hydrides. In addition, atomic halogen beams could be used to etch semiconductor and other materials in a uniform, well controlled manner. Other areas of interest, such as fundamental surface science and chemical kinetics, are obvious. It is also possible to generate beams of molecular particles with the present invention although the primary use for the present invention is the production of single atom particles. For simplicity, the term atom beam, when applied to the present invention, is assumed to include the whatever particle is desired from the source even if the desired particles are molecules. There are several systems that are presently available for the above applications, but they are, in general, quite large, expensive, not ultrahigh vacuum (UHV) compatible, and require the samples to be brought to their location.

In U.S. Pat. No. 4,828,817 a process for generating a pure atomic oxygen beam was disclosed, which process obviated many of the disadvantages associated with the systems of the prior art. Still lacking, however, was a simple workable, practical device that is small and designed for UHV applications.

SUMMARY OF THE INVENTION

It is accordingly the primary object of the present invention to provide what is not available in the prior art, viz., a small, vacuum compatible hyperthermal (energy=0.1 eV) atom generator which is simple, yet eminently practical and workable.

This object and its attending benefits were achieved by the provision of an instrument which combines the mechanisms of O_2 dissociation and transport of oxygen atoms through a hot Ag membrane to provide a continuous source of O atoms to a vacuum interface where they are subsequently emitted into the vacuum space by electron stimulated desorption (ESD) or photon stimulated desorption (PSD). A flux of neutral O atoms on the order of 1x10^13 cm^-2 s^-1 (P) with a kinetic energy of approximately 5 eV and a FWHM of 4 eV generated in UHV is now possible. The geometry of the instrument is such that it is mounted on a 7-cm flange and can be tailored in length and orientation to fit most UHV systems. The data presented here are for ESD-controlled conditions where increases in the flux are strictly linear with electron bombardment current. Transport controlled conditions can be achieved at temperatures as low as 350°C with membrane thicknesses on the order of 10 μm.

The instrument of the present invention includes a membrane having two sides, the membrane having the capability of dissolving the atoms into its bulk. If no other means of dissociation of the gas species is provided, the membrane must also have the capability of dissociating molecules of the desired gas species into atoms. The gas species includes any precursor molecule or atom which will yield the desired atom beam in the present invention. The membrane material is chosen to allow the dissociation of the atoms and for ESD characteristics eg. Ag for an O source, Pd for H source, Ta for N source. A means is provided to expose a first side of the membrane to molecules or previously dissociated atomic species, and another means provides a vacuum environment of a pressure of less than 1x10^-1 Torr on the second side of the membrane. A heater affords a temperature sufficient to promote dissociation of the molecules (if a prior means of dissociating the molecules is not provided) and the subsequent atomic permeation to the second side of the membrane. The heater can include any device or method that raises the temperature of the membrane above ambient temperature eg. electric resistance heater, electron beam heater, quartz lamp heater. The exciting means (electron or photon source) can also serve as the heater. An exciting
means excites the atoms to a non-binding state, resulting in their release from the second side of the membrane as an atomic beam. Optionally, a predissociation means dissociates the source molecules prior to or in conjunction with their adsorption on the first side of the membrane. The predissociation means may consist of any means that yields a higher concentration of dissociated or electronically excited species in the gas phase or on the membrane surface than would be obtained without the predissociation means eg glow discharge, RF plasma, photon source, catalytic surfaces, microwave plasma. The exciting means may advantageously consist of a cathode (any source of electrons) as well as a lens system if the geometry of the cathode requires a lens system. The cathode and lens system may be circular or any other shape that accomplishes the bombardment of the membrane surface with electrons. A lens system is any device that affects the trajectories of charged particles. The lens system is primarily for directing the electrons to the surface of the membrane in a generally uniform coverage, but the lens system may also optionally limit the escape of charged species from the source. One possible lens system that would accomplish this purpose consists of one or more grids in the path of the atom beam. The lens system can include electrode surfaces, insulating surfaces, or grids. An electrode surface is any conductive surface that has the capability, when electrically charged, of affecting the trajectories of charged particles. A grid is any mesh constructed of conductive materials that is capable of affecting the trajectories of charged particles when electrically biased.

The exciting means may also include a photon source, either alone or in combination with the cathode and/or lens system. This configuration could also include an optical lens system which is any device that affects the paths of photons.

**BRIEF DESCRIPTION OF THE DRAWINGS**

For a more complete understanding of the present invention, including its primary object and attending benefits, reference should be made to the Description of the Preferred Embodiments, which is set forth below. This description should be read together with the accompanying drawings, wherein:

FIG. 1 is a schematic representation of the combined mechanisms of predissociation, transport through a membrane followed by emission of hyperthermal neutrals according to the present invention. A is representative of the atomic species desired eg O, N, H, Cl, F;

FIG. 2A is a schematic of a device according to the present invention, FIG. 2B is a detailed inset showing a top hat membrane, a circular cathode, and a reflector of the device of FIG. 2A. FIG. 2C is a detailed inset showing an example of another possible cathode configuration in which the cathode is placed directly above the membrane surface, and FIG. 2D is an detail inset showing an example of the present invention using a photon source for the exciting means;

FIG. 3A is a Simion computer simulation of the electron trajectories for another possible cathode/lens assembly configuration, and FIG. 3B is a Simion computer simulation showing that highly energetic secondary electrons have trajectories which return to the emission plane showing the ability of this particular lens system to limit the escape of charged species from the source;

FIG. 4A is a Simion computer simulation of ion trajectories for a sample to target distance of 9 cm, and FIG. 4B is a Simion computer simulation showing that when a bias of -80 V is applied, all ions return to the emission plane;

FIG. 5 shows the atomic oxygen signal for a device according to the present invention designed for atomic oxygen production as detected by a quadruple mass spectrometer (QMS);

FIG. 6 is a plot of atom flux as a function of electron bombardment current for a device according to the present invention designed for atomic oxygen production;

FIG. 7 is a plot of O signal vs. time showing that upstream removal of O\textsubscript{2} has an ultimate effect on atomic oxygen flux for a device according to the present invention designed for atomic oxygen production;

FIG. 8 is a plot showing the ion energy distribution for electron stimulated desorption (ESD) from Ag and pure Ag and an Ag 0.5 Zr alloy according to the present invention designed for atomic oxygen production;

FIG. 9A shows an appearance potential curve for examination of the internal state of O neutrals from a device according to the present invention designed for atomic oxygen production, and FIG. 9B is a Simion computer simulation for estimation of the field leakage for a device according to the present invention having the specific geometry shown in FIG. 2B; and

FIG. 10 is a plot showing the initial steady-state atomic oxygen flux for a device according to the present invention designed for atomic oxygen production, followed by removal of the incident electron beam, followed by turning the electron beam on again after five minutes.

FIG. 11 is a plot showing the advantageous effect of predissociation on transport for the O/Ag system.

**DESCRIPTION OF THE PREFERRED EMBODIMENTS**

The hyperthermal atom generator (HAG) of the present invention employs two different mechanisms. The first is the permeability of atoms through solid materials (eg O in Ag, O in Yttria stabilized, ZrO\textsubscript{2}, H in Pd, N in Ta) sequential adsorption of gas molecules (or atoms if a predissociation means is used) surface dissociation into atoms (if necessary), dissolution into the bulk, and diffusion of atoms through a membrane where the atoms emerge at the vacuum interface and enter into atomically bound states at the surface. At sufficiently high temperatures, the atoms which arrive at the vacuum interface have sufficient thermal energy for surface diffusion which ultimately results in recombination and desorption of molecules. Optionally, a means for predissociation may be included to enhance the transport rate. The second mechanism is the utilization of electron-stimulated desorption (ESD) or photon stimulated desorption (PSD). By using an incident flux of electrons or photons, the bound atoms are excited to antibonding states and desorb as neutrals with kinetic energies greater than 0.1 eV (eg 5 eV for 0 ESD from Ag). Fig. 1 shows the combination of these two processes schematically. Usually, ESD and PSD are conducted on coated surfaces where the emission is a function of the decay in surface coverage. Eventually, the coverage becomes so low that redosing is required to continue the study. In the present invention, a continuous source of gas species (A\textsubscript{y}, where 1 < x < 8) is provided (upstream), usually 0.1 < p < 1000 Torr, to resupply the vacuum interface (downstream) by permeation through a membrane 13, e.g., Ag or Ag alloy of thickness <0.254 mm for an O source, Pd or Pd alloy for H source, Ta or Ta alloy for N source. This, of course, means that the membrane 13 must be operated at a temperature high enough to ensure a sufficient permeability, but yet low enough that the atomic adsorbed state is stable, and molecular species are not formed.
plate 25 minimizes membrane or target contamination prior to transmission through this quadrupole mass filter. At an energy of 2 eV or greater are detected. Clearly, the predominant bombardment over membrane 13, which will generate a dense secondary electron cloud due to the impact of energetic secondaries. The ionized efficiency for this QMS was determined from operation at +50 V with respect to the cathode, which gives the uniform bombardment flux as shown. FIG. 3B shows that even highly energetic secondary electrons (1000 eV) have trajectories which return to the surface of membrane 13 in the potential field shown. Very energetic positive ions (10 eV) which are emitted by ESD in this potential field are, in part, going to reach target 36 located 10 cm away. As is shown in FIG. 4A, the ions emitted in parallel paths near the centerline of membrane 13 (normal to the surface of membrane 13) have sufficient energy to escape the potential field of reflector 29. However, if a bias voltage of −80 V is applied to membrane 13, the maximum excursion away from the membrane is 9 cm, so the ions would not arrive at a target 36 or a sample 10 cm away, thus effectively trapping all ion emission within that distance (see FIG. 4B). Further, this bias does not affect the ESD of neutrals in any significant way. A separate electrode in front of the emission plane to capture all the ions is also an option, but it is desirable to minimize any scattering or recombination surfaces which may alter the emission flux or purity.

The spectra of a hyperthermal atom generator according to the present invention, particularly an atomic oxygen generator, as detected by a quadrupole mass spectrometer (QMS) with the ionizer in the appearance potential mode and the extractor voltage at OV, is shown in FIG. 5. The QMS signal due to background gases cuts off at extractor potentials less than 2 V, which indicates that ions with energies less than 2 eV have a negligible probability for transmission through this quadrupole mass filter. At an extractor potential of 0 V the ESD neutrals are detected, but background signals are not. This indicated that ESD neutrals of 2 eV or greater are detected. Clearly, the predominant peak is atomic oxygen. The continuously diminishing peak at m/e=19, which is most likely H₂O from the QMS ion source, ultimately disappears after sufficient cleanup. The ionized efficiency for this QMS was determined from

\[
\frac{J_{e}}{J_{m}} = \frac{S}{\text{QMS sensitivity}} \frac{k_{p} r}{\text{target area}} \frac{V_{e}}{A_{p}}
\]

where S is the QMS sensitivity, kₚ is Boltzmann’s constant, T is the gas temperature, A is the area of the aperture, e is the electronic charge, and Vₑ is the velocity of the entering particles. Equation (2) yields an efficiency of \(6.4 \times 10^{-5}\) ions/atom for an emission current of 0.2 mA. This ionizer sensitivity was used to calculate an 0 neutral/0 ion ratio of 1.6x10⁷. This very high 0 neutral/O ion ratio may be a result of a dense secondary electron cloud due to the impact of the primaries (Eₑ~1700 eV). The emitted ESD ions then...
experience a high probability of neutralization. The variation in atomic oxygen flux as a function of incident electron flux is shown in FIG. 6. The linearity seen is consistent with normal ESD behavior and indicates that the hyperthermal oxygen atom generator of this invention is ESD limited in this case. The highest flux achieved so far with the atomic oxygen source is approximately 5 × 10^12 cm^-2 s^-1 (I_e = 20 mA) at a distance of 10 cm from the emission plane.

The dependence on the source of molecular oxygen upstream is shown in FIG. 7. A steady-state level atomic oxygen flux was first established at an upstream O_2 pressure of 100 Torr. The O_2 was then pumped out, and the atomic oxygen signal began to decay. After an arbitrary overnight interval of about 16 hours, the 100 Torr of O_2 was reapplied to the upstream side, and the original level of atomic oxygen flux was recovered. This confirmed the source of the atomic oxygen and demonstrated the tandem behavior of the two basic mechanisms of oxygen transport and ESD emission. Adjustment of the upstream pressure of O_2 is an optional method of controlling the atomic flux, but is not nearly as quick or easy as adjusting the incident electron flux. From FIG. 7 it is seen that of O_2 upstream has an ultimate effect on atomic oxygen flux, but over 14 hours is required to decay a factor of 10.

The ion energy distribution for ESD of oxygen from pure Ag (curve "a") and Ag 0.5 Zr alloy (curve "b") is presented where Q is the ESD or PSD cross-section where K is the permeability. FIG. 8 shows the ion energy distribution for ESD of oxygen from pure Ag (curve "a") and Ag 0.5 Zr alloy (curve "b") is presented in FIG. 8. An estimate of the neutral distribution was accomplished by varying the lens voltage in the QMS from OV (where the background gases are expelled) to +10 V where the most energetic oxygen neutrals are expelled. It was found that the mean energy for the neutrals is greater than 2 eV. It is suspected that the distribution is quite similar to the ion distribution which is consistent with the hypothesis that the emitted ions by ESD are neutralized by the secondary electron fog with very little loss of kinetic energy.

It appears quite likely that 1 × 10^12 cm^-2 s^-1 is achievable before reaching a transport or diffusion limited condition. The cross-over point from ESD control to diffusion control can be easily estimated. FIG. 10 represents the initial steady-state atomic oxygen flux (a), followed by the removal of the incident electron beam (b), and finally the beam being turned back on five minutes later (c). No change in the magnitude of the flux was observed (d), which indicates that the surface coverage was not changed, and therefore, that the hyperthermal oxygen atom generator used is capable of generating ESD limited data. This is consistent with the data shown in FIG. 6. The transport of atoms through a membrane (J_t) at steady-state is given by

\[ J_t = \frac{2KP^2}{d} \exp \left( -\frac{E_F}{RT} \right) \]

where K is the permeability, P_o is the normalized upstream pressure (atmospheric fraction), d is the membrane thickness, E_F is the activation energy for transport, T is the membrane temperature, and K_o is the membrane permeability. The flux of ESD or PSD (J_{ESD}) emitted neutrals and ions at steady-state is given by

\[ J_{ESD} = QN \eta \]

where Q is the ESD or PSD cross-section N is the oxygen concentration, and J_e is the incident electron or photon flux. At steady-state when d_0/d = 0, then and the temperature where this occurs is given by

\[ T_c = \frac{E_F}{R} \left( -\log \left( \frac{2KP^2}{d} \right) \right)^{-1} \]

At 5 mA incident e- flux, a value of T_e = 406°C is determined for the cross-over temperature for the O atom source, which for this membrane thickness (0.038 cm) is acceptable.

Increasing the incident electron flux to 50 mA to proportionally increase the atomic oxygen flux to J_e = 1 × 10^13 cm^-2 s^-1, gives a cross-over temperature of 513°C, which is too close to the temperature for molecular desorption, it then becomes desirable to reduce the membrane thickness to d = 13 μm (this Ag film thickness requires a support structure) where the cross-over temperature becomes a more acceptable T_c = 365°C.

FIG. 11 shows the effect of predissociation on the overall transport rate of atoms from the high pressure side of the membrane to the low pressure side. At approximately t = 5 minutes, a glow discharge was initiated in the gas species supply. The effect of the glow discharge is to dissociate the gas species into atoms, thereby changing the rate at which adsorption and desorption into the bulk take place. The net effect is nearly an order of magnitude increase in the overall transport as shown in the figure. At t = 28 minutes, the glow discharge was turned off and the transport eventually returned to the original level. As is understood by those of skill in this art, variations and modifications in this detail may be effected without any departure from the spirit and scope of the present invention, as defined in the hereto-appended claims.

We claim:

1. A vacuum compatible hyperthermal atom generator, which comprises:
   - a membrane having two sides, the membrane having the capability of dissolving atoms into the membrane's bulk;
   - a first housing in operative association with the first side of the membrane to provide for the exposure of the first side of the membrane to a gas species;
   - a second housing in operative association with the second side of the membrane for providing a vacuum environment having a pressure of less than 1 × 10^-3 Torr on the second side of the membrane; and
   - exciting means for exciting atoms adsorbed on the second side of the membrane to a non-binding state so that a portion from 0% to 100% of atoms adsorbed on the second side of the membrane are released from the second side of the membrane primarily as an atom beam.

2. The vacuum compatible hyperthermal atom generator of claim 1 wherein the exciting means includes a cathode in operative association with the membrane.

3. The vacuum compatible hyperthermal atom generator of claim 2, further including a lens system for directing electrons from the cathode to the surface of the membrane in a generally uniform coverage.

4. The vacuum compatible hyperthermal atom generator of claim 3 wherein the cathode is a circular cathode and the lens system is a circular electrode positioned concentrically in the vicinity of the circular cathode.

5. The vacuum compatible hyperthermal atom generator of claim 3 wherein the lens system has a grid positioned in the vicinity of the cathode the grid being capable of affecting trajectories of charged particles when electrically biased.
6. The vacuum compatible hyperthermal atom generator of claim 5 including a plurality of grids.

7. The vacuum compatible hyperthermal atom generator of claim 3 wherein the lens system has an electrode surface in the vicinity of the cathode.

8. The vacuum compatible hyperthermal atom generator of claim 7 including a plurality of electrodes.

9. The vacuum compatible hyperthermal atom generator of claim 2 wherein the cathode is a filament.

10. The vacuum compatible hyperthermal atom generator of claim 9 wherein the filament is selected from the group consisting of tungsten, tantalum, iridium, thoriated tungsten, thoriated iridium, thoriated tantalum, and thoriated tantalum.

11. The vacuum compatible hyperthermal atom generator of claim 2 wherein the cathode is a field emitter.

12. The vacuum compatible hyperthermal atom generator of claim 2 wherein the cathode is a circular cathode.

13. The vacuum compatible hyperthermal atom generator of claim 2 wherein a portion of the cathode is positioned within a volume defined by the projection of the surface of the second side of the membrane in a direction generally perpendicular to the surface of the second side of the membrane.

14. The vacuum compatible hyperthermal atom generator of claim 1 wherein the exciting means includes a photon source in operative association with the membrane.

15. The vacuum compatible hyperthermal atom generator of claim 14, further including a lens system for directing photons from the photon source to the surface of the membrane in a generally uniform coverage.

16. The vacuum compatible hyperthermal atom generator of claim 14, further including an optical lens system for directing photons from the photon source to the surface of the membrane in a generally uniform coverage.

17. The vacuum compatible hyperthermal atom generator of claim 1 wherein the gas species is a member selected from the group consisting of O₂, N₂, H₂, Cl₂, F₂, and I₂.

18. The vacuum compatible hyperthermal atom generator of claim 1 wherein the membrane is selected from the group consisting of silver and silver alloys, tantalum and tantalum alloys, palladium and palladium alloys.

19. The vacuum compatible hyperthermal atom generator of claim 1 further including a grid, at least a portion of the grid being capable of affecting trajectories of charged particles when electrically biased.

20. The vacuum compatible hyperthermal atom generator of claim 19 including a plurality of grids.

21. The vacuum compatible hyperthermal atom generator of claim 19 wherein the grid is constructed of materials selected from the group consisting of silver and silver alloys, gold and gold alloys, tungsten and tungsten alloys, tantalum and tantalum alloys, palladium and palladium alloys, and iridium and iridium alloys.

22. The vacuum compatible hyperthermal atom generator of claim 1 including a heater in operative association with the membrane for providing a temperature sufficient for the promotion of an effective amount of atomic permeation to the second side of the membrane.

23. The vacuum compatible hyperthermal atom generator of claim 22 wherein the heater is located within the first housing.

24. The vacuum compatible hyperthermal atom generator of claim 1 wherein at least a portion of the heater is located within the second housing.