ИСТОЧНИКИ СПОНТАННОГО ИЗЛУЧЕНИЯ И ИХ ПРИЛОЖЕНИЯ

ULTRAVIOLET EXCIMER RADIATION FROM NONEQUILIBRIUM GAS DISCHARGES AND ITS APPLICATION IN PHOTOPHYSICS, PHOTOCHEMISTRY AND PHOTOBIOLOGY

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Narrowband UV and VUV excimer radiation can be generated in a variety of nonequilibrium gas discharges: dielectric barrier discharges, microhollow cathode discharges, arrays of microplasmas, corona discharges. Excimer lamps (excilamps) are now available for a large number of wavelengths and in various geometrical shapes. The availability of nearly monochromatic photon fluxes ranging in energy up to 15 eV resulted in a number of innovative photo-induced processes in photophysics, photochemistry and photobiology. This report focuses on progress made in the last decade.

Keywords: *ultraviolet radiation, excimer fluorescence, photochemistry, materials processing, pollution control, phototherapy.*

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Introduction

Sources of incoherent excimer radiation, excimer lamps or excilamps, have recently gained considerable importance. They can provide high photon fluxes mainly in the ultraviolet (UV) or vacuum ultraviolet (VUV) part of the spectrum. Typical efficiencies are at least an order of magnitude higher than those of excimer lasers. Progress has been made in understanding and optimizing the discharge physics and reaction kinetics of excimer formation. In addition to the already established technologies of UV curing, materials processing and pollution control novel applications like nanoparticle charging, particle coating and single photon ionization (SPI) of organic molecules emerged. Several manufacturers now offer excimer lamps for various industrial applications and as research tools. This report focuses on developments that took place in the last decade. For the extensive literature on earlier developments the reader is referred to a number of review papers on the subject [1–7]. The most comprehensive information on excimer lamps can be found in a recently published book by Boichenko, Lomaev, Panchenko, Sosnin and Tarasenko [8].

Different Discharges

The most important non-equilibrium discharge used for the generation of excimer radiation is without doubt the dielectric barrier discharge (DBD). In DBDs the requirements for efficient excimer formation (high electron energy at reasonably high pressure and comparatively low gas temperature) can easily be fulfilled. Different electrode geometries for generating filamentary or diffuse volume DBDs with one or two dielectric barriers and coplanar systems with buried adjacent electrodes leading to surface discharges are common. Scale-up is straight forward and cost-effective reliable power supplies are available. This technology, originally developed for industrial ozone generation, has been described in several reviews [1–8] and will not be repeated here. In laboratory studies also radiofrequency [9, 10] and microwave excited DBD excimer lamps [11–13] have been studied. A very simple configuration is the use of two parallel sleeve or ring electrodes placed on the outside of a dielectric tube. At about atmospheric pressure and narrow electrode spacing surface discharges are initiated at the inner surface of the tube [14, 15]. At reduced pressure of about 10 hPa a fairly wide separation of the external sleeve electrodes (up to 38 cm) can be used to sustain a glow discharge inside the tube. This configuration is often referred to as a capacitive excilamp [16, 17]. Straight cylindrical as well as bent U-shaped tubes are used. Power supplies providing bipolar meander pulses at 100 kHz repetition frequency are typically used.

It should be mentioned that excimer formation has also been obtained in several other types of high-pressure non-equilibrium discharges. Microhollow cathode discharges are important examples [18–20]. In a pulsed Xe microhollow cathode discharge efficiencies of 20% were reached [21]. The discharge behaviour of a Xe microhollow cathode discharge was modeled by Boeuf 2005 [22]. In addition, discharges in metal capillaries can emit excimer radiation [23] and also dc excited cathode boundary layer (CBL) discharges can produce intense Xe excimer radiation [24]. In a similar way microplasmas produced in narrow holes or slits can be used [25, 26]. Also arrays of several microplasmas were investigated [27, 28]. A completely different approach uses dc corona discharges from a number of pins in planar configurations or from a central wire in cylindrical configurations as a simple and efficient source of excimer radiation [29, 30].

Electron Beam Pumped Excimer Lamp (EBEL)

A compact sealed rare gas excimer VUV source based on electron beam excitation was first described by Wieser in 1997, 1998 [31, 32] and further investigated by Fedenev [33], by Morozov [34, 35] and by Ulrich [36]. An electron beam of about 10–20 keV energy is generated in a small vacuum chamber with the aid of a heated tungsten filament. Accelerated electrons pass through an extremely thin (300 nm thick) vacuum tight silicon nitride (SiN_x) membrane into a second chamber filled with a rare gas at about atmospheric pressure. For electron energies above 12 keV the losses in the membrane amount to only a few percent. In the rare gas the electrons are slowed down over a short distance exciting atoms which immediately form excited dimers. The second excimer continua of Ar, Kr, Ne, Xe can be obtained with striking energy efficiency (about 30% for Ne, Ar and about 40% for Kr, Xe). The gas volume excited in 1000 hPa Ar is about 1 mm^3, an almost spherical region of bright VUV excimer radiation. The Ar_2^*, Kr_2^*, Xe_2^* radiation can be extracted through a MgF_2 window. This excimer lamp can be run in dc or pulse mode. The SiN_x membrane will hold up to a pressure difference of more than 5000 hPa, a dc beam current of 10 μA, or a pulse current of 2 A for 100 ns. This compact source of excimer radiation has been commercialized under the name e-lux™ [37] and is used as a soft ionization source in advanced mass spectrometry.

Pulsed Excimer Lamps

An interesting property of many excimer systems is hat they can be run at high power densities. Bright pulsed excimer flash lamps have been reported in the literature. In 1996 Kubudera described a pulsed DBD using a mixture of Kr and Xe in pulsed DBD to obtain broadband VUV emission ranging from 120 nm to 190 nm from the dimers Kr_2^*, $XeKr^*$ and Xe_2^* [38]. A few years later this group reached a radiant power density of 1.5 kW/cm^2 VUV output peaking at 147 nm from a pulsed Kr DBD [39]. This was achieved with a filamentary DBD in a quartz tube with external linear strip electrodes on opposite sides (6 mm wide, 600 mm long). Carman focused on short pulses with high repetition rates (up to 50 kHz) and reached VUV efficiencies of 60% in a diffuse Xe DBD [40]. The peak radiant power density was 6 W/cm^2. Tarasenko [41] showed that with a nanosecond duration runaway electron preionized diffuse discharge (REP DD) in all atmospheric pressure rare gases VUV radiation from the second excimer continuum could be obtained. Best results were obtained in Xe with a radiant peak power of 300 kW corresponding to a 1.5 kW/cm^2 radiant power density at the output window. At an elevated pressure of 1.2 MPa the Xe_2^* peak radiant power density could be raised to 6 kW/cm^2 for an 8 ns pulse. The electrical power density during the pulse was 100 MW/cm^3 [41]. The technology of REP DD was discussed in detail by Baksht [42]. Short-pulse excitation of near atmospheric pressure Ne was studied by Carman using a DBD with current pulses of 150 ns duration [43]. Almost monochromatic radiation of Ne_2^* peaking at 84 nm was obtained with 5 nm FWHM (full width at half maximum). High values of radiant peak power densities can also be obtained in the rare gas/halogen systems Kr/Cl_2, Xe/Cl_2, Kr/Br_2 and Xe/Br_2 [44, 45]. In these systems radiant power densities of a few kW/cm^2 were obtained at efficiencies close to 5%. Typical operating parameters were total pressures of 650–1000 hPa and halogen admixtures of 1 to 2% [41]. In addition to high radiant power densities or high repetition rates pulsed excimer lamps can also be optimized for other characteristics. For example, a miniaturized XeCl lamp with a fast decay of the UV radiation, about three orders

of magnitude within 5 μs, was developed with intended applications in fluorescence spectroscopy for the detection of biomolecules [46, 47].

Open Discharge Configurations

The Xe excimer lamp is by far the most important VUV lamp because its photon energy of 7.2 eV is high enough to initiate various photochemical processes and special sorts of fused silica glass (quartz) have high transmission at 172 nm, so that sealed lamps of high life expectancy can be produced. For shorter wavelengths special windows have to be used (e. g. CaF_2, MgF_2, LiF) which are expensive and available only in smaller sizes. To circumvent this problem and still make use of the radiation of the Ar_2^* excimer radiation at 126 nm open discharge configurations, "windowless excimer lamps", were designed, in which the DBD for generating the VUV radiation and the substrates to be treated are both situated inside a through-flow reactor. The idea was first published by Kogelschatz in 1992 [1]. Photo-induced metal deposition was demonstrated starting from thin Pd acetate films [48]. The design of windowless excimer systems was followed up by several authors [49–51]. The most sophisticated design was recently published by Sobottka [52]. In this publication an atmospheric pressure glow discharge in Ar is run between parallel dielectric-covered electrodes of 540 mm length. The operating frequency was 680–840 kHz, the maximum electric power 20 kW. Substrates could be placed on a moving conveyor belt below the discharge. With well designed aerodynamic seals and an Ar flow of 4–6 m^3/h the residual O_2 content was <10 ppm in the zones exposed to VUV irradiation of the second Ar excimer continuum. The obtained irradiance was up to 30 mW/cm^2. Miscellaneous samples for both surface modification and surface activation were treated. The wavelength range of open sources was further extended to the EUV range in a pulsed Ne DBD running at 900 hPa [43]. In this investigation the second Ne excimer continuum peaking at 84 nm of 5 nm FWHM was obtained. There is no doubt that these open excimer sources provide entirely new possibilities for VUV induced processes.

Rare Gas Excimers

Excimer lamps based on the emission of rare gas excimers are probably the most important incoherent sources of VUV radiation. There are a number of reasons for this. Rare gas dimers are very efficient converters of discharge power or electron beam power to VUV radiation, theoretically up to 80%, in practice about 40–60%. These systems can be pumped to extremely high electrical power densities and there is practically no self absorption of the generated radiation. At pressures around 1000 hPa only the second excimer continua are excited which arise from an optical transition of excited diatomic molecules (excited dimers or excimers) from vibrationally relaxed $^1\Sigma_u$ and $^3\Sigma_u$ states to the repulsive ground state of the pure rare gases. Due to the structure of these transient molecules the radiation is restricted to a narrow wavelength region. Table 1 gives the electron energy and wavelength at peak intensities and the spectral width (full width at half maximum: FWHM) at a typical pressure of about 1000 hPa.

Table 1. Second Excimer Continua of the Rare Gases

Dimer	He_2^*	Ne_2^*	Ar_2^*	Kr_2^*	Xe_2^*
Peak (eV/nm)	15.5/80	14.8/84	9.8/126	8.4/146	7.2/172
FWHM (nm)	20	5	9	11	14

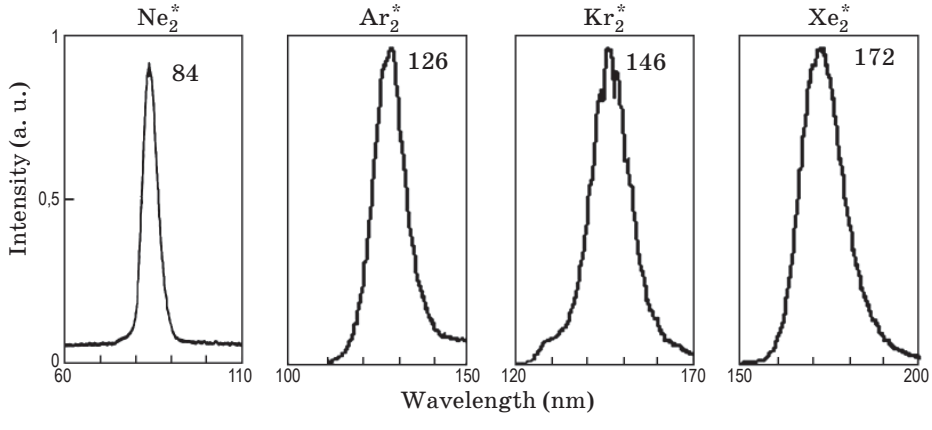

Fig. 1. Spectra of Rare Gas Dimers.

Kinetic Models of Excimer Formation

Due to the importance of Xe excimer lamps there have been extensive modeling efforts using extended kinetic schemes. Carman [53, 40] comes to the conclusion that short pulse excitation is necessary to obtain high VUV efficiency. This 1D kinetic model showed that about 60% of the discharge energy can be converted to VUV radiation, mainly the second excimer continuum at 172 nm, while 38% is lost in thermal heating. Contributions of visible and infrared radiation are negligible. This group also showed that increasing the Xe fill pressure favored high peak power generation. The pulse energy deposited in the discharge could be increased and the VUV pulse duration could be shortened due to a faster conversion of Xe^* excited states into the VUV emitting Xe_2^* dimers. Above 1500 hPa, the experimental VUV pulse widths approached the theoretical lower limit of 68 ns, set by the lifetime of the triplet excimer state $Xe_2^*(^3\Sigma_u^+)$, the main source of the 172 nm emission.

Bogdanov simulated the discharge development in pulsed Xe DBD lamps first in a 1D approach [54] and later in a 2D model [55]. The role of the displacement current during cathode sheath formation is discussed and its importance for efficient formation of excited Xe^* atoms. Lo [56], simulating the Xe_2^* VUV fluorescence of a 50 ns pulsed discharge in pure Xe at the high reduced power density of 7 $MWcm^{-3}$ bar^{-1}, used more or less sophisticated kinetic schemes and came to the conclusion that an extended theoretical model with nine electronic Xe levels gave the best description of the experimental data.

Avtaeva and Kulumbaev [57] also presented a 1D hydrodynamic model for calculating the characteristics of xenon excilamps. Avtaeva and Skornyakov [58] investigated the implications of using more sophisticated nonlocal electron kinetics. The local field approximation for the electron energy used in many of the previous publications was replaced by solving the electron energy balance equation. This resulted in significantly thinner space charge layers, stronger fields and enhanced ionization close to the dielectric walls. More recently these authors compared simulated and experimental data obtained at 400 hPa Xe with sinusoidal feeding voltage at 15 kHz for a 2 mm discharge gap and a 4 mm gap [59]. For these operating conditions they obtained two short current pulses for each half-wave of the applied voltage and predicted VUV efficiencies of 50% for the 2-mm gap, up to 80% for the 4-mm gap. In both cases the contribution of the 147 nm resonance line was about 1% only.

Beleznai [10, 60, 61] compared experiment and modeling of three different excitation modes: 250 ns pulses, 1000 ns pulses and gated 2.5 MHz bursts. This group used a cylindrical silica glass tube with external linear strip electrodes of 1.5 mm width and 100 mm length. The inner diameter of 9.65 mm resulted in a comparatively wide discharge gap. Stability of a diffuse volume discharge could be obtained at pressures up to 250 hPa. Typical measured VUV efficiencies were around 60%, in the simulations up to 70% were reached. The authors also looked at the construction of Xe_2^* based fluorescent lamp by using a glass tube with an internal phosphor coating for the conversion to visible light. With a green phosphor ($LaPO_4$:Ce,Tb) they achieved a lamp efficacy of about 75 Lm/W. Belasri [62, 63] using an additional circuit model and a fine mesh in the sheath region investigated DBDs in Ne/Xe mixtures over a large frequency range and studied the influence of operation voltage, dielectric capacitance, gas mixture composition, operating pressure, and that of secondary electron emission at the cathode on the generation of the Xe_2^* radiation.

In conclusion it can be said the Xe excimer system is very efficient and reasonably well understood. There is common agreement that energy dissipated by ions is lost energy not leading to excimer formation. Most authors propose to use short discharge pulses or high frequencies to minimize ion motion. The main channel leading to Xe_2^* is via the excited atomic levels Xe(1s4) and Xe(1s5) produced by direct excitation from the ground state and by collisional deactivation of higher lying levels. While the majority of authors concentrate on the time domain to optimize the system there is an alternative approach using a simple dc discharge and careful design of two locally separated regions, a small ionization region for electron and ion production and an optimized electron drift region for efficient excitation. Salvermoser and Murnick [29, 30] achieved 50% efficiency for the second Xe excimer continuum in a negative dc corona discharge and estimated a theoretical limit of 87%.

The second system that has been extensively investigated is the formation of $XeCl^*$ exciplexes in mixtures of Xe, perhaps with additional other rare gases, and a chlorine donor like Cl_2 or HCl.

The kinetics of binary and ternary gas mixtures leading to $XeCl^*$ formation had been thoroughly investigated in connection with XeCl excimer lasers. With the availability of commercial powerful $XeCl^*$ excimer lamps using DBDs more recent publications focus on the numerical modeling of discharge processes in such lamps. Bendella [64] studied breakdown in a Xe-Ne-HCl excimer lamp initiated by successive electron avalanches at the cathode which are propagated in the sheath with a high field. Ionization is mainly due to direct electron impact but also due to the metastable species accumulation in the gap. Belasri [65, 66] treated the formation of the cathode sheath in a Ne-Xe-HCl mixture and the influence of secondary electrons released by ion impact and by 172 nm photons. Avtaeva [67] recently proposed a numerical model for Xe/Cl_2 mixtures. Addition of 1% molecular chlorine to xenon resulted in getting 90% of the radiation on the $XeCl^*$ B-X transition at 308 nm with a discharge UV efficiency of 26% for a total pressure of 330 hPa and sinusoidal feeding voltage at 100 kHz. In general it can be stated that halogen/rare gas excimer lamps can also be run at much lower pressure, e. g. 10 hPa, because fast two-body reactions like harpooning reactions of excited atoms and ion recombination reactions are important. Efficient excitation of the second continua of rare gases on the other hand requires higher operating pressure, typically above 100 hPa, because the main pathway leading to excited dimers is a three-body reaction involving an excited atom and two ground state atoms. It should be mentioned that many more excimer systems have been investigated in laboratory studies, e. g. excimers radiating in the visible spectral range, multi-wavelength excimer sources and white color systems [68, 69].

Table 2. Important Rare Gas/Halogen Exciplexes (The spectral width of the B-X transition increases at reduced pressure)

Exciplex	$ArCl^*$	$KrBr^*$	$KrCl^*$	$XeBr^*$	$XeCl^*$
Peak (eV/nm)	7.1/175	6.0/207	5.6/222	4.4/282	4.0/308
FWHM (nm)	2	2	1.7	1.9	2

Resonant Energy Transfer and Lyman Alpha Lamp

The sensitivity of some rare gas dimers to the presence of impurities can be utilized for a very special lamp emitting radiation at 121.6 nm. This extremely narrow line radiation is due to the $2p^2P_0–1s^2S$ transition of a hydrogen atom and is normally referred to as the Lyman-α line. It can be obtained in He or Ne with traces of hydrogen. It has been obtained in e-beam pumped lamps with an energy efficiency of about 10%, in a microhollow cathode discharges [70] and in a DBD type discharge with an efficiency of a few percent [14]. Typically less than 0.1% H_2 was added to He or Ne at a pressure of 400 to 1000 hPa. The line width was determined by tunable diode laser absorption spectroscopy [71]. It is surprisingly narrow. At a total Ne pressure of 1000 hPa it amounts to 3.85 pm FWHM. The excited $H^*(n = 2)$ atom is formed by resonant dissociative excitation of H_2 by excited He or Ne species. There has been some debate about the exact reaction mechanism in Ne. In principle two main reactions are conceivable.

While earlier publications [14, 15, 31, 70], based on the experimental observation that the

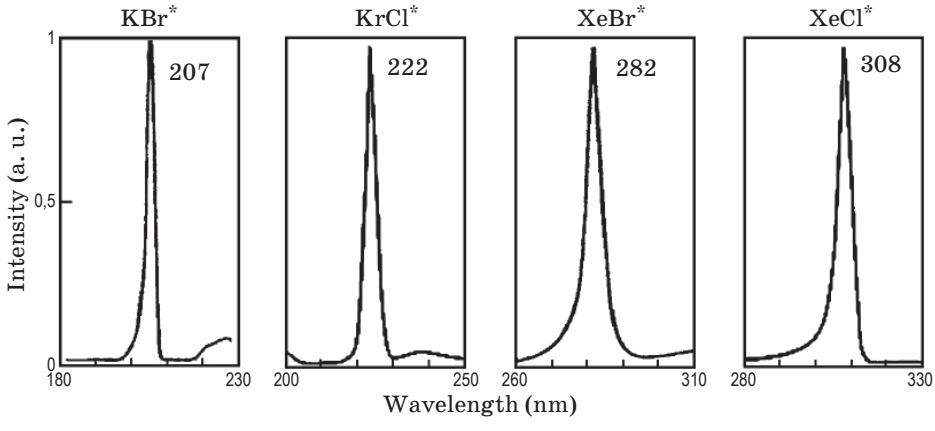

Fig. 2. Spectra of some Rare Gas/Halogen Exciplexes.

second excimer continuum disappeared upon addition of traces of hydrogen, assumed energy transfer from the excited dimer Ne_2^*, more detailed later investigations of Morozov [72] came to the conclusion that excited Ne^* atoms are the main precursors for Lyman-α radiation. This is in agreement with model calculations of the Ne/H_2 mixture by Karelin and Yakovlenko who concluded that energy transfer from Ne^* is in fact the major reaction channel leading to H^* formation [73, 74]. They arrived at an energy efficiencies of 6% when less than 10 hPa H_2 is added to 1000 hPa Ne. In experiments an optimum concentration of about 0.01% H_2 in 1000 hPa Ne was determined [72].

The Lyman-α lamp has very attractive features. It provides a clean emission spectrum with an isolated sharp line at 121.6 nm (10.2 eV) at reasonable intensity and efficiency. This wavelength falls into an absorption window of oxygen and might even be used in atmospheric air. With DBD excitation using sleeve electrodes on the outside of a dielectric tube and operating at 13.56 MHz stable optical VUV outputs of 8 W have been reported [75]. Applications are expected in photolithography [14, 76], in microstructured metal deposition and for nanofabrication [77].

Other examples of resonant energy transfer have also been reported. When traces of O_2 are present the second Ar_2^* excimer continuum peaking at 126 nm easily transfers its energy to a narrow OI line at 130.3 nm, which actually is a triplet [15, 78]. Volkova and Gerasimov observed energy transfer from the second Kr_2^* excimer continuum peaking at 146 nm to the Xe resonance line at 147 nm [79–81]. In Ar discharges energy transfer from the atomic $^3P_1$, $^3P_2$ states of argon and from the excited Ar_2^* dimers to atomic nitrogen lines (149.47 nm, 174.52 nm) was observed [82]. Traces of H_2O (0.02%) in Ar lead to efficient selective excitation of the OH band ($A^2\Sigma^+ \rightarrow X^2\Pi$) close to 310 nm by energy transfer from the 4s states of Ar^* to H_2O molecules with subsequent dissociation [83]. In all these selective energy transfer processes surprising overall efficiencies of a few percent are reached.

Commercial Excimer Lamps

Many companies now offer excimer lamps. Some should be mentioned. Ushio Inc. of Japan was one of the first companies pioneering excimer lamp technology and now has a large collection of excimer lamps: 126 nm (Ar_2^*), 146 nm (Kr_2^*), 172 nm (Xe_2^*), 222 nm ($KrCl^*$), 282 nm ($XeBr^*$), 308 nm ($XeCl^*$). Linear cylindrical lamps up to 2 m length and assemblies of lamps in larger excimer irradiation units are available for industrial applications. Flat excimer lamp systems with window sizes of 300 mm diameter or 152×152 mm square (CiMax™ Excimer Lamp System) are mainly used in the semiconductor industry and reach UV irradiances of 50 to 100 mW/cm^2 with a uniformity of 2.5%. Smaller VUV units are available for research applications. The German company Heraeus Noblelight GmbH, another pioneer in commercializing excimer lamps, offers a similar collection of high power cold UV excimer systems. Osram of Germany marketed an extremely efficient pulsed Xe excimer lamp under the name of Xeradex™. This cylindrical lamp is now available up to 625 mm in length, an electrical power of 100 W and a VUV efficiency of 40%. All these lamps use DBD excitation. A different type of xenon excimer lamp using a dc corona discharge is offered by UV Solutions Inc. in the US [84]. This company developed a cylindrical lamp of 595 mm length, 50 W electrical power and efficiency up to 50%.

The availability of powerful UV and VUV sources prompted a large number of research activities in photo-induced processes, some of which already made it to the market. The largest number of excimer based lamps is however used in the form of external electrode rare gas fluorescent lamps, a special DBD configuration, used in photocopiers, scanners and for LCD backlighting. The operating gas is a mixture of Xe and Ne, similar to that used in plasma display panels (PDPs), the operating pressure slightly below atmospheric. Internal phosphor coatings are used to convert the 172 nm radiation of the Xe excimer to the near UV or visible spectral range. Such Xe based fluorescent excimer lamps for photo, film and video lighting and for mercury free image processing lamps in scanners and in copying and fax machines are now manufactured by different companies: XeFl™ lamps by Ushio, Linex™ (linear excimer lamp) and Planon™ (planar excimer lamp) by Osram. The Planon™ claims a life expectancy of 100 000 hours.

VUV Photolysis of Oxygen and Water Vapor

For the photo-dissociation of strongly bound molecules like O_2 and H_2O the incoming photon has to be absorbed and has to be energetic

enough to break the bond. This requires wavelengths shorter than 200 nm. In principle the 185 nm line of low pressure mercury lamps and also the radiation of deuterium lamps can be used. With the advent of much more powerful VUV sources like the Xe excimer lamp entirely new perspectives were opened. Its photon energy of 7.2 eV is sufficient and the absorption cross sections of O_2 and H_2O at 172 nm are high: $\sigma(O_2) = 6\times10^{-19}$ cm^2, $\sigma(H_2O) = 4\times10^{-18}$ cm^2. The first process yields an O atom in the ground state O(^{3}P) and a very reactive excited atom O(^{1}D). In pure oxygen at low conversion and fast gas flow both atoms will finally result in ozone formation with a yield approaching 2 O_3 molecules per VUV photon [85]. The photodissociation of H_2O at 172 nm leads to the formation of an H atom and a hydroxyl radical OH with a quantum yield close to one [86]. For liquid phase water photohomolysis (OH radical production) in methanol (0.2–0.3 M) solution at 172 nm a quantum yield of $\Phi(OH) = 0.42 \pm 0.04$ was determined [85]. In pure gases the pertinent reactions are as follows [87]:

$$h\nu + O_2 \rightarrow O(^1D) + O(^3P), \quad (1)$$

$$O(^1D) + M \rightarrow O(^3P) + M, \quad (2)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M, \quad (3)$$

$$h\nu + H_2O \rightarrow H + OH. \quad (4)$$

If gases, O_2 and H_2O vapor, are present the situations gets much more complicated. Even traces of humidity have a strong influence on the reaction kinetics. Additional reactions of importance are:

$$H + O_2 + M \rightarrow HO_2 + M, \quad (5)$$

$$OH + O_3 \rightarrow HO_2 + O_2, \quad (6)$$

$$HO_2 + O_3 \rightarrow HO + 2O_2, \quad (7)$$

$$OH + HO_2 \rightarrow H_2O + O_2, \quad (8)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2, \quad (9)$$

$$H_2O_2 + OH \rightarrow H_2O + HO_2. \quad (10)$$

Depending on their concentrations and absorption cross sections also photo-dissociation of secondary species like H_2O_2, OH, HO_2 has to be considered.

VUV Surface Cleaning and Conditioning

The reactions described in the previous section are the base of a photochemical process of surface cleaning and surface modification which is of immense industrial importance in material sciences, in semiconductor and display technology and, more recently, also in nanotechnology. VUV cleaning with sets of long Xe excimer lamps has become the final contact-free cleaning step for the large glass plates and glass ceramics used in LCD (liquid crystal display) and PDP (plasma display panel) manufacturing [88–90]. In addition the process is used in many other cleaning applications for Si wafers, lenses, mirrors, reticle plates [91], quartz oscillators and also metal parts like terminal tabs for flat TVs, IC wire bonding and micro motor shafts, to mention only a few examples. The aim is to remove the last residues of hydrocarbon and water based contaminants and to condition the surfaces for the next production steps. In this process a combined action of 172 nm photons with an aggressive chemistry based on the photodissociation of traces of O_2 and H_2O in a UV transparent carrier gas (Ar, N_2) is used. The active species are O(^{1}D), O(^{3}P), OH, HO_2 in addition to O_3 and H_2O_2. Due to the high absorption coefficients of O_2 and H_2O at 172 nm the trace concentrations can be adjusted in such a way that the short-lived radicals are generated close to the surface to be treated. The contaminants are converted to volatile products like CO, CO_2, NO_2 and H_2 that can be carried away in the gas flow. At the same time highly hydrophilic functional groups, such as –OH, –CHO and –COOH, can be incorporated into the surface to condition it for subsequent coating or bonding steps. Additional examples for specialized VUV cleaning processes using also other excimer lamps can be found in the recent review of Oppenländer [92].

VUV Induced Surface Modification

Many polymer surfaces can be modified or even ablated through the action of ultraviolet radiation in passive or reactive atmospheres. Controlling this etching process is of importance for the semiconductor industry (resist ashing), for materials processing and for nanofabrication technologies [93]. The Xe excimer also found widespread applications for the surface activation of polymers, for photochemical matting and microstructuring of acrylate-based coatings

[94, 95]. Adding nano-silica and micro-corundum particles to such acrylate coatings led to markedly improved scratch and abrasion resistance [96]. The conversion of polysilazane layers into dense silica or methyl-silica structures was also demonstrated with Xe excimer lamps [97, 98]. The more energetic Ar excimer radiation can be used for direct cleavage of the C-H bond in polymers, for room temperature oxidation of Si or SiGe [99] and for the direct nitridation of metal oxides [100]. The Ar excimer radiation peaking at 126 nm has the extraordinary capability to split N_2 molecules and to generate highly excited $O(^1S)$ atoms from O_2.

In addition, modern research concentrates on the VUV-induced modification of surface properties of polymers that are used extensively in medicine or biology to enhance their biocompatibility. More recent research activities focus on the control of surface properties with respect to biocompatibility. For example, cell adhesion could be achieved on PTFE (polytetrafluoroethylen) and novel nanocomposite polymer surfaces modified by VUV irradiation in an ammonia atmosphere with a Xe excimer lamp [101, 102]. Such aminofunctional surfaces are now widely used for the attachment of biomolecules. They can be patterned by using the same Xe excimer lamp for the photodegradation of the condensed films in certain preselected areas [103].

Excimer UV Radiation in Air and Water Purification

Considering the extensive literature on the use of different excimer lamps in pollution control, disinfection and surface decontamination one gets the impression that the majority of these lamps are used in destructive photochemistry or photodegradation. The target substances are either attacked by UV photons directly or by highly reactive species generated by UV photons. An exhaustive treatment of the use of excimer lamps in pollution control was given by Oppenländer in the book "Photochemical Purification of Water and Air" [104] and recently expanded and updated in a review article [7] and in his chapter "Excilamp Photochemistry" in the CRC Handbook of Organic Photochemistry [92]. A typical example is the use of advanced oxidation processes (AOPs) in which H, OH, and HO_2 radicals play a dominant role in addition to O_2, O_3 and H_2O_2. This process is used, for example, to treat biologically toxic or non-degradable materials is waste waters by removing contaminants such as pesticides, aromatics, and volatile organic compounds (VOCs). A critical review of the processes initiated by the 172 nm VUV radiation of a Xe excimer lamp in water was given by Gonzalez [86]. One of the drawbacks is that this radiation is absorbed in a very thin surface layer (less than 100 μm). As a consequence, excimer lamps with longer wavelengths like KrCl at 222 nm and XeBr at 282 nm are also used in water treatment [105].

UV Charging and Coating of Nanoparticles

Nanoparticles and nanostructured composites find increasing applications in industry and as biocompatible surfaces. Coated nanoparticles are investigated for usage in biomedical applications. Therefore the generation, handling and processing of nanoparticles has attracted much attention. Excimer lamps have found applications in charging, in surface modification and in coating procedures of nanoparticles. Particles in the size range below 100 nm can efficiently be charged by a process called UV charging or photocharging [106–108]. The process depends on the photoemission of electrons and leaves positively charged nanoparticles with up to 25 elementary charges. It works with metallic and dielectric nanoparticles. KrCl and Xe excimer lamps have been engaged. Such photochargers are used in differential mobility analysers and in real time PAH (Polycyclic Aromatic Hydrocarbon) monitors to analyse Diesel off gases [109].

The repulsion of nanoparticles with unipolar charges prevents agglomeration and is helpful in processing individual nanoparticles. Oxidation of polystyrene aerosols was demonstrated with a Xe excimer lamp [110]. In atmosphere containing oxygen and traces of H_2O the surface of submicron size polystyrene particles was functionalized by hydroxylation and the incorporation of carbonyl groups. Zhang, also using a Xe excimer lamp, showed that thin polymer coatings, less than 20 nm thick, could be applied to NaCl particles ranging from 20 to 60 nm in diameter [111]. Boies succeeded in coating silver nanoparticles with a silicon dioxide SiO_2 layer by photoinduced chemical vapor deposition (photo-CVD) using TEOS (tetraethylorthosilicate) as precursor and a Xe excimer lamp for its dissociation [112].

Single Photon Ionization (SPI)

VUV radiation from excimer lamps has also found interesting applications in analytical chemistry. VUV radiation from the Kr or Ar second excimer continua can be utilized for soft ionization of many organic compounds. This technique of single photon ionization (SPI) of complex organic molecules without or with only minor fragmentation of the original molecule opened entirely new prospects for mass spectrometry (MS) in on-line, real-time process gas analysis [113, 114]. Using a compact EBEL excimer VUV source with an Ar filling about 70 different photoionization cross sections of organic compounds were recently determined [115]. The Ar excimer continuum peaking at 9.8 eV from a compact EBEL source was used for single photon ionization and combined with a time of flight mass spectrometer (SPI-TOF-MS) coupled to gas chromatography for fast and reliable determination of photoionization cross sections (PICS). The sensitivity for certain compounds in the 10 ppb range is so high that it now appears possible to use SPI/MS techniques in airports for trace detection of security relevant substances like explosives and illegal drugs. Other applications are expected in environmental monitoring, in medicine (breath analysis) and in industry for process control and quality control [116].

Excimer UV Phototherapy

Excimer lamps have also found applications in phototherapy and photochemotherapy. Phototherapy typically uses UVB radiation (280–315 nm) while photochemotherapy uses radiation in the UVA range (315–400 nm) combined with an oral dose of psoralen, a coumarin based photosensitizer (PUVA therapy). Typical examples are the treatment of psoriasis, alopecia areata, vitiligo, atopic dermatitis and eczema. Many medical treatments that have been originally developed with mercury lamps or XeCl excimer lasers can also be performed with excimer lamps. In many cases the treatment is less expensive and in some cases also more specific. A number of recent investigations used $XeCl^*$ excimer lamps with radiation peaking at 308 nm and FWHM of 2 nm for large area treatment of skin diseases [117–121]. In the medical literature this is often referred to as MEL (monochromatic excimer light) therapy. A number of such units already made it to the market: “Excilite” by DEKA in Italy, “Quantel Derma” by DermOptics in France, “VTRAC” by PhotoMedex in the US and “TheraBeam UV308” by Ushio in Japan. Ushio uses an additional filter to suppress short wavelength radiation. An alternative approach is to use a Xe based excimer fluorescent lamp with a suited UV phosphor. More detailed information on the use of excimer lamps in phototherapy can be found in the reviews of Oppenländer [92] and Tarasenko [122].

Outlook

Excimer lamp technology developed rapidly during the last two decades. In many cases mercury free and novel alternatives emerged to conventional UV lamps. VUV excimer lamps opened entirely new possibilities in surface cleaning, surface modification, in UV curing and in coating processes. Current activities target advanced processes like the micro and nanostructuring of polymer surfaces, surface functionalization of carbon nanotubes and of nanoparticles and the advancement of nano-imprint lithography, to mention only a few examples. Encouraging laboratory results have been obtained with different excimer UV lamps in the field of air and water purification. While biological and medical applications are still in its infancy further progress is expected in understanding and controlling the interaction of UV photons and/or excited and ionized species with living cells. It is probably fair to say that excimer lamps have reached a degree of maturity, their potential for future photochemical and technological applications is obvious, but further progress is required in the development of adequate process technologies.

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