UV SOURCES – Basics, Properties and Applications

WOLFGANG HEERING

Lichttechnisches Institut, University of Karlsruhe, Kaiserstrasse 12, D-76131 Karlsruhe, Germany;
wolfgang.heering@lti.uni-karlsruhe.de

ABSTRACT

Ultraviolet (UV) radiation is produced mainly by gas discharge lamps and light-emitting diodes (LEDs). Gas discharge sources are principally low pressure mercury lamps, manufactured as standard, amalgam or high output lamps, medium pressure mercury lamps, doped high pressure lamps, rare gas high pressure lamps and excimer lamps. These lamps strongly differ in dimension, spectral range, specific electrical power, radiant efficiency, lifetime and coupling to a power supply. Rather new developments are electrodeless medium frequency mercury induction lamps and some low pressure molecular gas discharge lamps, which emit in the UVB and UVA. The history of LEDs, which have a UV output beyond 100 mW, is just at the beginning. The structure and radiation mechanism of such UV LEDs will be presented. UV lamps are used not only in the field of disinfection of water, air and surfaces, but also for curing UV colors, lacquers and anti-corrosion layers, for advanced oxidation technologies to decompose pollutants in air and water and for therapeutic treatments.

KEYWORDS: UV LEDs; UV discharge lamps; UV applications; UV efficacy

BASICS

Up to now, nearly all ultraviolet (UV) lamps generate radiation by means of a gas discharge. They are produced with lengths varying between a few centimeters and four meters, specific electrical power between 0.1 W/cm and 400 W/cm, spectral emission from the deep vacuum UV (VUV) up to the long-wave UVA, radiant efficiencies between a few percent up to 60% and lifetimes from some hundred hours up to many thousands of hours. In a gas discharge, electrons are accelerated by an electric field of 1 to 100 V/cm. By collisions with atoms, molecules or ions, electrons, they transfer kinetic energy and excite some of the heavy gas particles; part of them return from excited states to states of lower energy under spontaneous emission of radiation. After some reabsorption, internally emitted radiation will pass though the lamp envelop to the outside. Among the most efficient UV radiators are low-pressure (LP) mercury lamps, made with either quartz glass or borosilicate (soft) glass, and medium pressure mercury lamps with a bulb of quartz glass and filled with much larger amounts of mercury and often also with certain dopants. If the mercury pressure is of the order of only 1 Pa, re-absorption is weak, and so the resonance lines at 184.9 and 253.7 nm are the principal ones emitted by a LP mercury lamp. Under these conditions, the ratio of the resonance line intensities is then about 1:5.

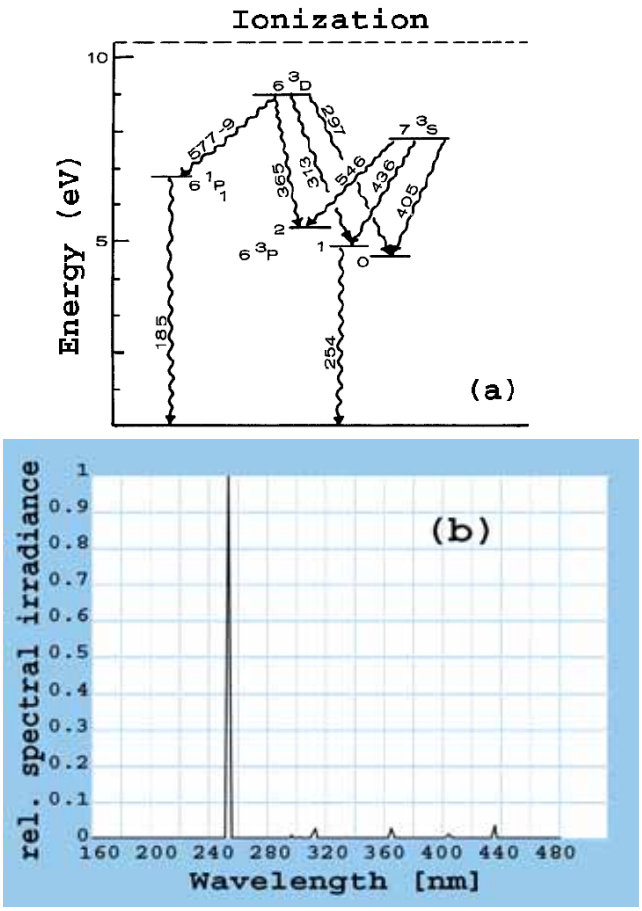

Figure 1. (a) Energy level diagram of mercury with probable radiant transitions and **(b)** UV spectrum of a standard low pressure lamp (type NN, Heraeus Noblelight).

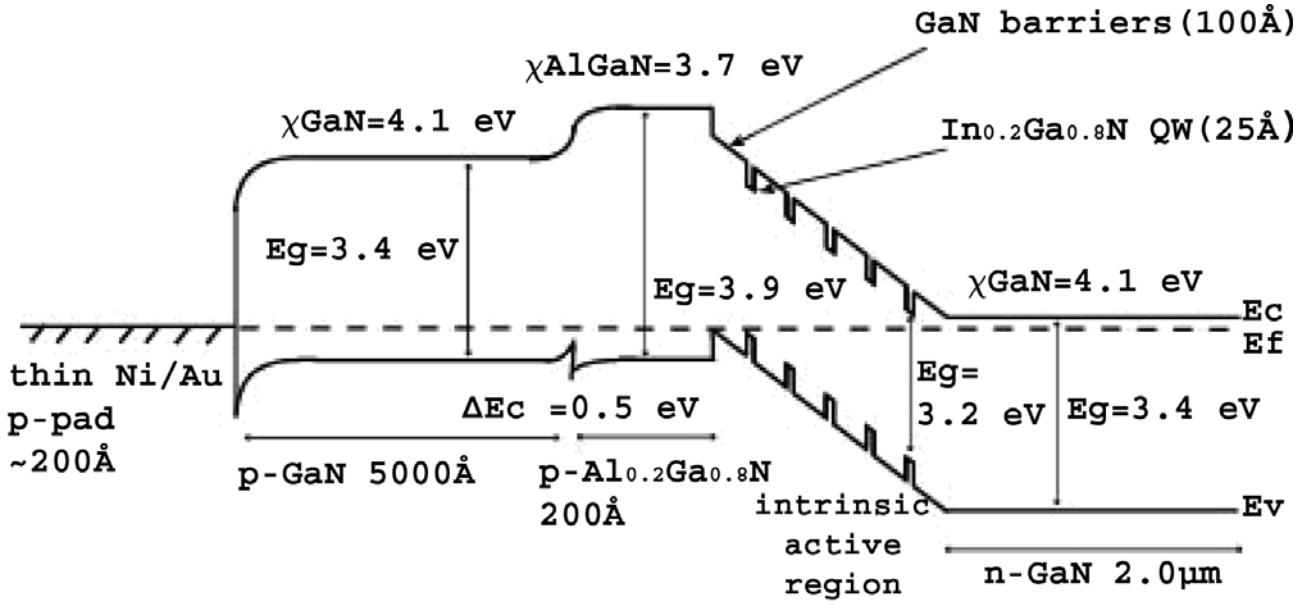

Figure 2: Energy band diagram of an InGaN MQW Blue LED (Grundmann et al. 2002).

The working principle of a UV light-emtting diode (LED) is demonstrated by an InGaN MQW Blue LED, as an example. Figure 2 presents the energy band diagram of such an LED. Applying a forward voltage bias to a semiconductor *pn* junction, electrons are injected from the *n*-type semiconductor (*n*-GaN) and holes from the *p*-type semiconductor (*p*-GaN) into the active layer (InGaN) between, the composition of which fluctuates and has a quantum well structure. Part of the injected carriers recombine within the quantum well under the emission of UV or blue radiation, if the band gap there is large enough. The UV radiation emerges through a wider band gap material (SiC or sapphire).

InGaN-BASED UV LEDs

III-V nitride based semiconductors have a direct band gap suitable for short-wave light-emitting devices. The bandgap energy for instance of AlGaInN varies with composition between 6.2 and 1.89 eV at room temperature. If the active layer of the LED is GaN or AlGaN, the efficiency of LEDs is very low because there are many nonradiative recombination centers. However, by adding Indium (In), localized energy states are formed in which electrons and holes are preferably captured where they recombine radiatively. Thus the output power of a UV LED containing a small amount of In in the active layer, with emission at 380 nm, can be about 20 times higher than that containing no In with emission at 368 nm. When the emission becomes shorter than 371 nm, the output power decreases strongly because of self-absorption of radiation by the adjacent *n*- and *p*-type GaN layers. Figure 3 shows the external quantum efficiencies (ratio of the UV power to the electrical power) of InGaN-based LEDs and the emission spectra of some LEDs in the UVA.

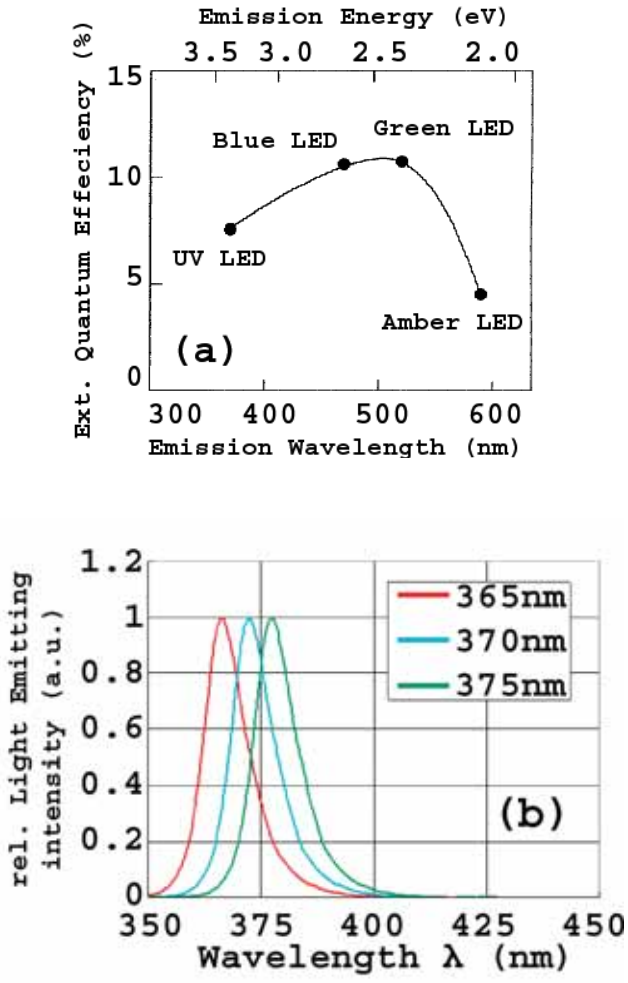

Figure 3: External quantum efficiencies and spectra of InGaN-based LEDs (Nakamura 1999).

Today surface-mounted UV LEDs are available with 100 mW radiant power output at 365 nm for a DC current of 500 mA and 4.5 V forward voltage at T_c = 25°C.

LOW PRESSURE GAS DISCHARGE LAMPS

The diffuse low pressure mercury lamp still has the highest UV radiant efficiency in air. The resonance line emission is at a maximum at a saturated mercury vapor pressure of 0.8 Pa for tube diameters of 26 and 38 mm, which is reached at a cold spot temperature of 315 K (42°C). Under such conditions, the radiant efficiency of the plasma at 254 nm can be up to 60% for an Ar buffer gas pressure of about 300 Pa and a current of 430 mA. Unfortunately, these optimum discharge conditions can be only maintained at quite low power densities < 0.5 W/cm. The specific radiant power at 254 nm will then reach about 0.2 – 0.3 W/cm. This value can be raised by about a factor of three, if a Bismuth/Indium amalgam is used instead of pure mercury, and the electrical power density can then increase up to 2 W/cm into a tube with a reduced diameter. The amalgam will provide for nearly the same mercury pressure at a lamp temperature that is about 40 K higher than the optimum vapor temperature at 315 K. Specific radiant UV powers of 0.5 W/cm, which are between those of standard low pressure mercury T5 lamps (0.2 W/cm) and amalgam T10 lamps (0.8 W/cm), are emitted from the so-called low pressure high output (LPHO) lamps (Altena et al. 2001). This is achieved at larger diameters of 26 or even 33 mm. Comparable with the development of fluorescent lamps, there is a trend to smaller mercury (5 mg) filling. Reduced fillings became possible using better methods of mercury dispensing and by a protective glass coating of Al_2O_3, CeO_2 or Y_2O_3, which prevents mercury penetration into the glass tube and thus helps to maintain the UV output.

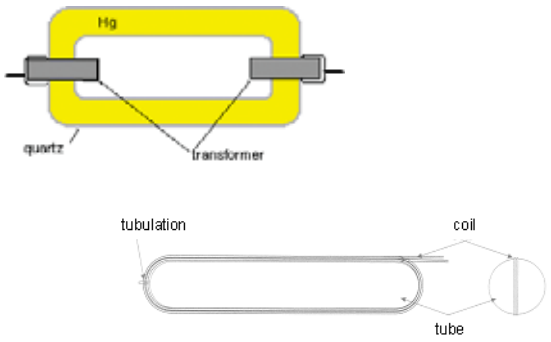

Figure 4: Two different designs of inductive coupling to a mercury LP lamp.

Radiant efficiencies at 254 nm for power densities up to 2 W/cm, which are comparable with those of amalgam lamps, can achieved using a new kind of low pressure mercury lamp, the low and respectively medium frequency induction lamp. These lamps have much longer life times of about 60,000 h, instead of 9,000 h for standard low pressure mercury lamps, because they do not contain electrodes in the interior of the bulb. The lamp type in the left half of Figure 4 has been developed by Godyak and Shaffer (1998) to be an efficient fluorescent light source and can be used as a UV lamp if the bulb is made of UV transmitting quartz glass. The lamp is a closed tubular ring that is driven by two externally mounted toroidal ferrite cores. Each ferrite core is provided with windings of wire connected to a 100 – 500 kHz power source. A 7.2 cm long lamp with diameter of 5.4 cm and filled with mercury and krypton as buffer gas is operated with high current of 7.1 A and discharge power of 138 W. The electrodeless LP mercury lamp in the right half of Figure 4 needs no ferrite cores with proper cooling structures. An induction coil with 2 – 14 turns is positioned on the outer tube wall in axial direction of the lamp with diameter of 5.0 – 7.6 cm and length of 30 – 50 cm. Popov et al. (2004) operated such lamps with frequencies between 250 kHz and 15 MHz and powers of 60 to 250 W. The efficiency decreases with the power coupled into the lamp.

For all LP mercury lamps there are many phosphors available that are deposited on the inner surface of the lamp bulb and transform the resonance line radiation to longer wavelengths in the UV. They are chosen so that desired therapeutic, cosmetic or curing effects of the radiation are at a maximum.

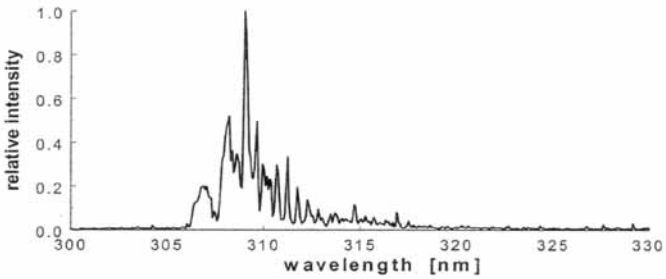

Figure 5: Molecular emission from the OH radical (Hilbig et al. 2004).

There are some other LP gas discharges that are free from mercury and emit in the UV. As Hatta (2004) has experienced, diffuse and stable discharges can be realized with carbon monoxide (CO) for a CO partial pressure of greater than 1000 Pa. They emit molecular radiation in the region from 150 to 210 nm. Other molecular discharges with broadband UV emission have been realized with sulfur as well as in water vapor (Figure 5: Hilbig et al. 2004). In water vapor, the UV radiation is from the A-excited state of the OH radical, which is created by electron collisions with water molecules and recombines with itself to water and oxygen. A new powerful mercury-free RF-excited low-pressure discharge, which emits a strong molybdenum spectrum in the UVB and UVA regions, has been developed by Giuliani and Petrov (2004). An RF power of up to 200 W is coupled by a spiral coil around the lamp at a fre-

quency of 13.56 MHz into a spherical bulb of 2.3 cm diameter which contains MoO_3 powder and Ar (at 2 mbar). Evaporative sublimation of the powder occurs at a wall temperature of about 800 K. The measured spectrum is shown in Figure 6.

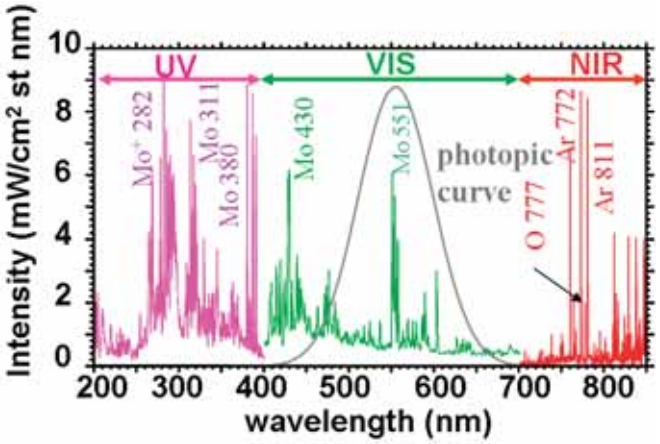

Figure 6: Spectrum of a RF excited Molyoxide-Argon discharge (Giuliani and Petrov 2004).

MEDIUM PRESSURE GAS DISCHARGES

Much higher UV power densities, up to 30 W/cm in the UV-C, can be obtained from mercury arc discharges that are operated at medium pressure of a few bar. Figure 7 presents the UV spectrum and estimated values of spectral radiance and irradiance (at a distance of about 10 cm) for a 4 kW high pressure mercury lamp with specific electrical power density of 200 W/cm and a bulb diameter of 2.6 cm. Such a lamp type is widely used for UV curing because the UV efficiency is fairly high. Lambrecht (1998) found that up to 14% of the electric lamp power is converted to UVC, about 7% into UVB and other 7% into UVA radiation. As demonstrated in Figure 8, the spectrum of a high pressure mercury lamp below the 254 nm resonance line can be strongly influenced by the mercury pressure which correlates with the specific lamp voltage. That means that the high current type will emit more radiation below 215 nm than the high voltage type at the same specific electrical lamp power. This may be explained by two effects. Firstly, an increasing part of the long-wave wing of the 185 nm mercury resonance line is reabsorbed with increasing mercury pressure. Secondly, the emission maximum at about 225 nm increases with increasing mercury pressure. This emission is generated by the radiative recombination of free electrons with mercury ions forming the metastable level 6^3P_2 excited state of the mercury atoms.

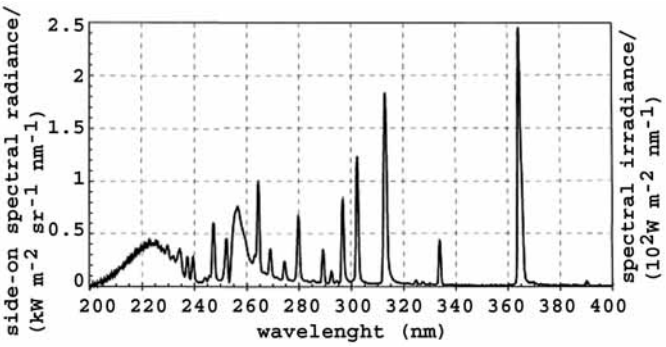

Figure 7: Spectral radiance and irradiance of a 4 kW HP Hg lamp with 200 W/cm.

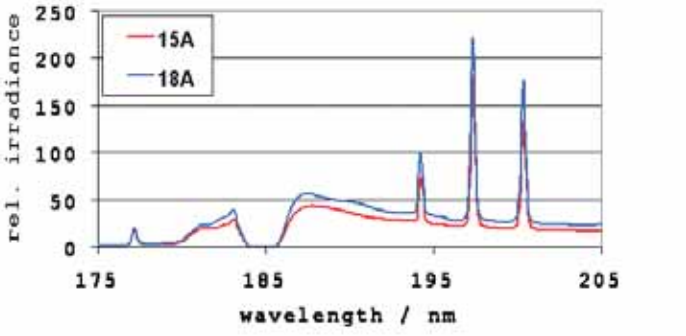

Figure 8: Enhanced VUV emission from a high current, medium pressure 2 kW mercury lamp with 100 W/cm (Körber and Heering 2004).

As large parts of the lamp power are emitted at wavelengths outside the germicidal range, the optimized medium pressure mercury lamp has a germicidal UV efficiency of only 12% (i.e., about one third of that of a low pressure mercury lamp). By using foils coated with molybdenum, using a better quality of quartz glass and operating lamps with an electronic power supply, the lifetime can be prolonged from 2,000 to 8,000 h.

By adding small amounts of silver (Ag), gallium (Ga), indium (In), lead (Pb), antimony (Sb), bismuth (Bi), manganese (Mn), iron (Fe), cobalt (Co) and/or nickel (Ni) to the mercury as metal iodides or bromides, the mercury spectrum can be changed strongly principally in the UV-A but also in the UV-B and UV-C. Doping Ga and In gives intense lines at 403 and 417 nm and at 410 and 451 nm, respectively. Iron iodide strongly raises the spectral radiant power by introducing many closely bunched iron lines in the range from 358 to 388 nm, which lowers the UV-B and UV-C efficiency significantly. Decreasing the UVC and partially the UVB is a general trend when iodides are added because they absorb principally the short-wave UV. However, in comparison to the pure mercury arc, the UV-A can be enhanced by up to a factor of 2 by iron and up to about 1.6 by manganese (Heering 2001).

Medium pressure discharges are operated with electrodes by means of a choke or transformer or are driven by an electronic power supply at higher frequencies. Electrode-free lamps can be energized by means of microwaves. We have experienced an intense emission in the spectral range of 340 – 420 nm from a kind of molecular lamp filled with CoI_2 and operated at a high load of 340 W/cm^3 using a microwave generator.

If extremely high but only transient UV irradiances and high penetration depths of radiation are needed, pulsed xenon high pressure lamps producing flash radiation in the UV, visible and intrared (IR) can be applied, for instance for curing highly pigmented and/or thick lacquer layers. Linear or circular tubes with lengths up to 500 mm are filled with xenon with pressures between 100 mbar and a few bar. Pulse energies from a few joules to more than 1000 joules are obtained from large capacitors which are discharged by the lamp. Discharge voltages are a few kV, pulse widths between 10 and 500 μs and pulse rate from 3 to 120 per second. Pulse peak powers may exceed 1 MW (Capobianco 2002). Beside spectral lines in the blue visible and in the near IR, an intense recombination continuum of radiation is emitted, which is described by a Planck curve with associated temperatures between 7,000 and 12,000 K. This can be raised and narrowed as well as shifted to shorter wavelengths with increasing current densities (up to 100 kA/cm^2). Though up to 60% of the energy input can be converted into radiation from 200 to 1000 nm, the germicidal efficiency is lower than that of LP mercury lamps and not higher than that of HP mercury lamps. The lifetime of such lamps is strongly dependent on pulse energy per volume and repetition rate. Depending on operating conditions, pulsed xenon lamps have to be replaced after 10^6 to 10^8 flashes.

EXCIMER LAMPS

A novel kind of high pressure gas discharge is the excimer lamp, which emits quasi-monochromatic radiation. Here, the electrodes are not positioned in the gas space, but they are separated by a dielectric barrier, usually quartz glass, from the gas. The coaxial quartz tube arrangement, shown in Figure 9, is quite often used because it is mechanically robust and can easily be manufactured. Inner and outer quartz tubes are connected with one another at the rims, and the volume between them is filled with a gas mixture for the desired formation of excimers (molecules that are stable only in the excited state). The outer electrode is a metal grid in order to transmit the radiation generated by the excimers in the gas space. Because of the dielectric barrier, a high alternating voltage of several kV with frequency between 30 and 500 kHz has to be fed to the outer electrodes. Thus many self-extinguishing micro discharges are generated at gas pressures about 1 bar under non local thermal equilibrium (NLTE) conditions. The micro channels are statistically distributed over time and space and exist only over times of about 10 – 20 ns. As the electric fields are quite high in the gap between the electrodes, even rare gas atoms can be excited efficiently by impacts with fast electrons. The excited rare gas atoms can then form excimers with other rare gas, metal or halogen atoms. These excimers dissociate with a corresponding emission having a width of 10 – 20 nm.

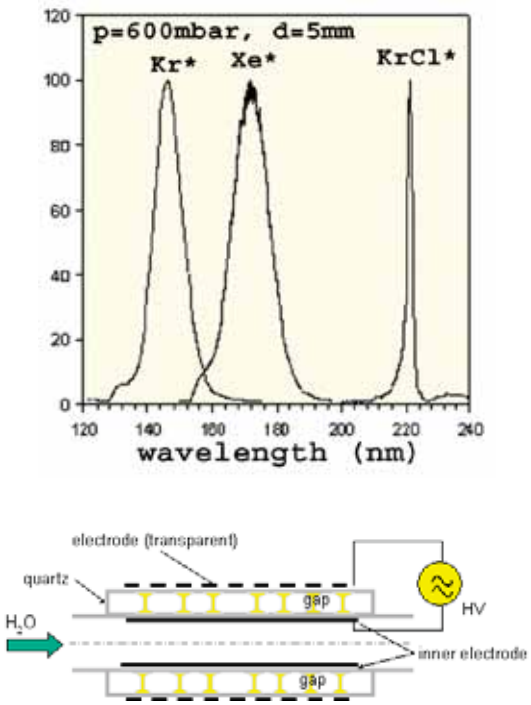

Figure 9: Coaxial excimer lamp geometry and spectra of Kr_2*, Xe_2* and KrCl*.

The most efficient rare gas halide systems are found to be ArF*, KrCl*, KrF*, XeBr*, XeCl*, XeF*, which emit at 193, 222, 248, 282, 308, 351 nm, respectively. In pure rare gas fillings, emission of Ar_2*, Kr_2*, Xe_2* is observed at 126, 146, 172 nm respectively (Figure 9). Radiant efficiencies of up to 14% respectively 18% are reported from commercial XeCl and KrCl lamps which are operated with an HF sinus drive (Altena et al. 2001). A more efficient excimer lamp is the Xe_2* dielectric barrier discharge if the electrical power input per unit of surface area is moderate. The electrical energy that is coupled into a micro discharge

must be limited if thermalization of electron energy is not to become the dominating process. Radiant efficiency can be further enhanced by a square wave shape driving voltage instead of a sinusoidal wave shape. Short-time records of the dielectric barrier discharge in xenon reveal that many more micro discharges are formed in a period during square wave operation. Hence, the energy per micro discharge is lowered and the radiant efficiency increased. Daub and Heering (2004) have experienced even higher efficacies of xenon dielectric barrier discharges if the voltage pulses are unipolar with rise and fall times of less than about 200 ns and pulse widths between 1 and 3 μs. Then the discharge reignites on the falling edge, further raising the radiant output. Thus UV irradiances at 172 nm with power densities up to 0.5 W/cm^2 can be produced with a lamp efficiency of about 20%. The lifetime of commercial xenon filled excimer lamps is now up to 5,000 h, and is not limited by any reaction between the quartz glass and the fill gas but by oxygen out gassing from the glass wall and by color centers that are formed in the quartz by low wavelength UV radiation. The xenon excimer radiation can be converted efficiently, by means of phosphors, into the germicidal spectral range. Preferably the phosphor contains praseodymium and lanthanum. Such a phosphor emits UVC radiation in two bands at 220 and 265 nm (Jüstel et al. 2002).

APPLICATIONS

First , the spectral emission of the lamp should be adapted to the photochemical process. Second, the actinic radiation should be produced efficiently. And last but not least, the maintenance and lifetime of the lamp must be guaranteed over thousands of hours. Often there is a trade-off between UV output per unit lamp volume and UV efficiency. This is realized especially in low-pressure mercury lamps, which are filled with a metal amalgam for a higher output per unit of arc length. Medium pressure mercury lamps, which emit the same UV power, can be made much more compact, though at the cost of lower disinfecting performance. LP mercury discharge lamps are mainly used for the disinfection of drinking water, as well as of surfaces, because the 254 nm resonance line is near the maximum of the action spectrum for disinfection at 265 nm. Medium pressure mercury lamps are applied for curing coatings in graphic arts and the automotive industry. UV curing gives high gloss, high chemical and high scratch resistance coatings at extremely short curing times. For highly pigmented and/or thick layers, an iron-doped medium pressure lamp may be the better alternative because UVA radiation is less strongly absorbed.

Medium pressure mercury lamps are also used in other fields of photochemistry; for example, the photolysis of: H_2O_2 (190 – 240 nm) giving hydroxyl radicals, O_3 (240 – 280 nm) yielding atomic oxygen, and C-F and C-Cl bonds (< 190 nm and 210 – 230 nm, respectively), etc. Excimer lamps produce nearly monochromatic radiation in the UV. The 282 nm radiation of the XeBr excimer lamp is surely the best choice for vitamin D_3 synthesis. The 172 nm radiation of the Xe_2 dielectric barrier discharge can remove polymers, activate surface bonds, adjust wetting angles, induce metallization and chemical vapor deposition (CVD) and directly dissociate molecular oxygen. By an appropriate phosphor, the 172 nm radiation can be efficiently converted into the spectral range of disinfection.

Furthermore, UV radiation is needed for the cosmetic treatment of the human skin as well as for phototherapy. Figure 10 shows some respective action spectra. UV lamps that are fit to such applications are fluorescent lamps with special phosphors and filtered metal halide short arc lamps.

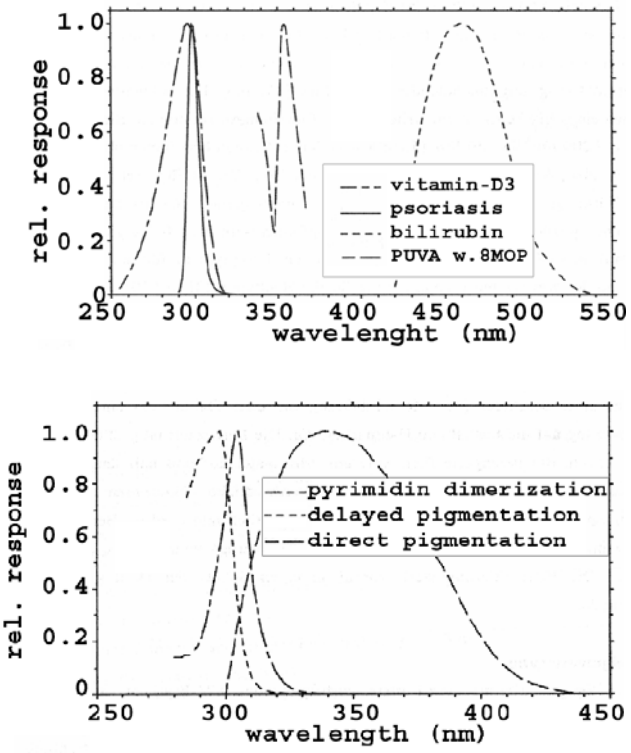

Figure 10: Action spectra of vitamin D_3 synthesis, psoriasis, bilirubin isomerization, photo-chemotherapy with PUVA (8-methoxypsoralen and UVA exposure), skin pigmentation and UV erythema.

REFERENCES

Altena, F.W., van Overveld, J.B.J. and Giller, H. 2001. Technological advances in disinfection lamps leading to more compact UV sources, Proc. 1st Int. Congress on Ultraviolet Technologies, Washington, DC, USA, International Ultraviolet Association, PO Box 1110, Ayr, ON, Canada N0B 1E0.

Daub, H.-P. and Heering, W. 2004. Vorrichtung zur Erzeugung von elektrischen Spannungsimpulsfolgen, insbesondere zum Betrieb von kapazitiven Entladungslampen, German Patent No. 10 2004 021 243.0 pending.

Capobianco, R.A. 2002. UV curing equipment for assembly applications, Application note AN-103, Xenon Corporation, Woburn, MA 01801, USA.

Grundmann, M., Haaheim, J., Moshar, A., and Summers, J. 2002. Blue InGaN Quantum Well LED Fabrication, University of California, Santa Barbara, CA.

Giuliani, J.L. and Petrov, G.M. 2004. Emission and kinetics of a moly-oxide-argon discharge bulb, Proc. 10th Int. Symp. on

Light Sources, Toulouse, France, p. 263-264, Institute of Physics Publishing, Bristol and Philadelphia, Conference Series No. 182.
Godyak, V. and Shaffer, J. 1998. Endura: A new high output electrodeless fluorescent light source, Proc. 8th Int. Symp. on Light Sources, Greifswald, Germany, p. 14-23, Institute for Low-Temperature Physics Greifswald (INP), ISBN 3-00-003105-7
Hatta, A. 2004. VUV emission from CO gas discharge, Proc. 10th Int. Symp. on Light Sources, Toulouse, France, p. 561-562, Institute of Physics Publishing, Bristol and Philadelphia, Conference Series No. 182.
Heering, W. 2001. Doped UV Arc Lamps – Performances and Limits of Operation, Proc. RadTech Europe 2001, Basle, Switzerland, p. 139-143, Vincentz Verlag Hannover, Germany.
Hilbig, R., Koerber, A., Baier, J., and Scholl, R. 2004. Molecular Discharges as Light Sources, Proc. 10th Int. Symp. on Light Sources, Toulouse, France, p. 75-84, Institute of Physics Publishing, Bristol and Philadelphia, Conference Series No. 182.
Jüstel, T., Nikol, H., Dirscherl, J., and Wiechert, D.U. 2002. Device for disinfecting water comprising a UV-C gas discharge lamp, US Patent No. 6,398,970 B1.
Körber, W.G. and Heering, W. 2004. Private communication, Lörrach and Karlsruhe, Germany.
Lambrecht, M. 1998. Untersuchungen an Quecksilberhochdrucklampen zur effizienten Erzeugung ultravioletter Strahlung, Dissertation, University of Karlsruhe, Karlsruhe, Germany.
Nakamura, S. 1999. InGaN-based violet laser diodes, Semicond. Sci. Technol. 14: R27–R40.
Popov, O.A., Chandler, R., and Maya, J. 2004. High power (100 – 200 W) ferrite-free electrodeless fluorescent lamp, Proc. 10th Int. Symp. on Light Sources, Toulouse, France, p. 173-*174, Institute of Physics Publishing, Bristol and Philadelphia, Conference Series No. 182.*