UV light - A powerful tool for surface treatment

Dielectric barrier discharge lamps at 172 nm and their use for cleaning, oxidation, etching and other surface modifications

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Light with sufficient energy has the ability to crack chemical bonds. Thus it is able to clean surfaces of organic contaminations or films by destroying the film chemistry. Vacuum UV (VUV) increases the surface energy and the wettability and helps to get better adhesion. VUV also cracks the O_2 in air and can be used to produce ozone and activated oxygen very effectively and locally for different aims. Surfaces like that of silicon wafers or other materials can be oxidized with very good quality and the simultaneous allocation of UV light speeds this process up even more effectively. The ability to destroy organic bonds can also be used to etch plastic surfaces, even PTFE, or to start chemical reactions without starter molecules like UV lacquers in printing industry.

Technical surfaces get dirty during production processes as well as during storage or transport. Mostly this “dirt” consists of water, organic substances like oil, oxides and/or salts. Additionally, surfaces can be coated by polymer films or oils for corrosion protection. Prior to further production steps it might be unavoidable to have to get rid of these surface contaminations.

Here, with Vacuum UV light, a powerful tool for surface cleaning will be presented. VUV systems can run at normal pressure, which means that the technical effort even for large surfaces is relatively low. VUV cleaning leads to perfectly clean surfaces without using solvents, which makes this process inexpensive and environment-friendly. It can be used for many different substrates like LCD panels, solar cells or plastics.

Cleaning – state of the art

The common way to clean surfaces is to wash with wet chemicals, e.g. water based, organic solvent or CFC or to clean using physical methods.

Physical cleaning methods are e.g. supercritical carbon dioxide, carbon dioxide snow or low pressure plasma cleaning. At sufficiently high film thickness on the surface, low pressure plasma cleaning can only be an additional cleaning step, but not a substitute for wet chemical cleaning steps. Usually it is the final step in a chain of different cleaning methods beginning with a wet process.

For plasma cleaning at low pressure (approximately in the 10^{-1} mbar range), a glow discharge will be generated by a high frequency electrical field. As the process gas, oxygen or other gases and gas mixtures are used. In the plasma, electrons, ions, active neutral species and UV radiation are produced which interact with the surface. Contaminations on the surface will be converted into volatile gases and in the end be removed by the vacuum system. Disadvantages of this method are the bombardment of the surface by highly energetic charged particles, which are undesirable especially on semiconductors, and the danger of breakdown through dielectrics. This can be overcome by different measures such as the use of afterglow plasma, but all of them increase process time.

Activating and etching

In principle the process is the same as for cleaning. Both chemical and physical methods can be used. Plasma processes are often used as well, but the parameters differ in process time, energy input and process gas.

Besides the above-mentioned plasma species used for cleaning surfaces, the chemically active species like radicals can

be different depending on the process gas. Plastic can be chemically activated, so that the surface gets higher surface energy and e.g. wettability. This is, for example, often needed to print on or glue plastic parts.
However, the disadvantages are similar. At higher energies or process times so many bonds in the plastic surface will be destroyed that the material will be etched away.

VUV cleaning

In opposition to plasma processes, with VUV treatment in the first instance only one species is produced – photons. The highly energetic photons emitted from VUV lamps are uncharged and do not have the momentum of accelerated ions. Increasing the treatment energy does not automatically increase the particle bombardment, ion implantation and surface perforation.

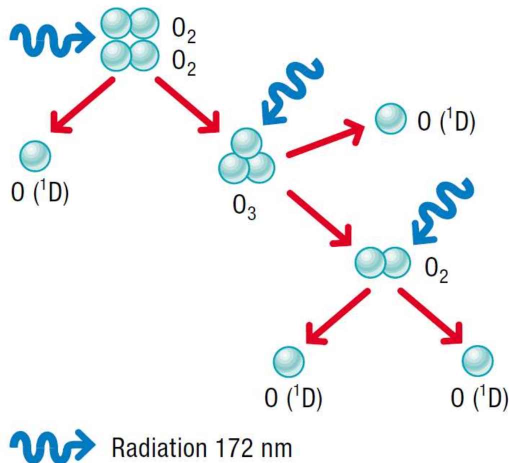

Fig. 1 *Ozone generation by UV radiation*

Active neutral species are produced additionally if a process gas is added in between lamp and substrate. The easiest example is the production of ozone and active oxygen if the process gas is air or pure oxygen (*Fig. 1*).
In the case of air there will be no additional production of NO_x. This is one of the main advantages of the use of 172 nm radiation.
Surfaces are cleaned with VUV radiation in the presence of air. The organic impurities are destroyed by the radiation, and together with ozone and active oxygen, CO_2 and H_2O are formed.
These volatile molecules are transported away together with the streaming air (Fig. 2).

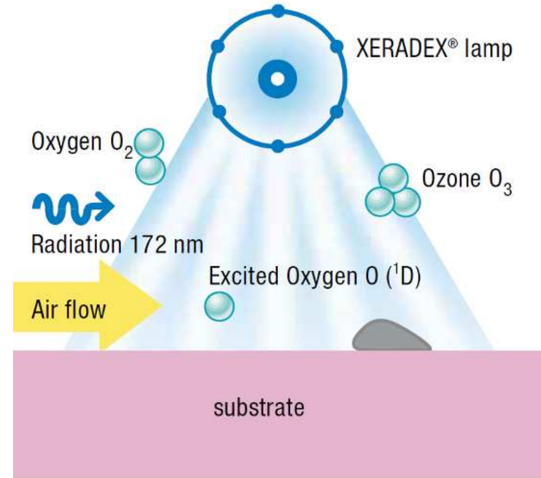

Fig. 2 *UV / ozone cleaning in air*

Altogether, VUV cleaning can lead to perfectly clean surfaces without any damages and without residues from the solvent or the impurity itself. No need to re-filter or dispose a lot of solvent saves money and protects the environment.

VUV surface activation

Even activating and etching are possible with VUV radiation like with plasma treatment, but with all the above-mentioned advantages.
For many industrial processes like gluing, printing on surfaces or preparing for various other coating methods, the surface of non-polar plastic surfaces in particular has to be activated. In the case of plastic, activating means the cracking of near-surface bonds and the addition of functional oxygen groups. There is also the fact that most activation methods like VUV additionally remove separating agents from the surface of molded plastic parts and therefore increase the adhesive strength of coatings or even make coating possible at all.
A similar, but chemically different, case is the activation of inorganic surfaces like SiO_2 or metals. Either because they are

already an oxide or because they have a native oxide layer, these materials cannot get functional oxygen groups. However, cleaning the surface and activation even in this case increases the surface energy and therefore decreases the surface contact angle markedly. This effect can last for hours, which makes it a useful tool in production.

Fig. 3 Water droplet on sawed silicon untreated (left) and treated for 2 s with UV / ozone (right)

VUV lamps

By far the most effective way to produce radiation in the vacuum UV region is the use of a dielectric-barrier-discharge (DBD) in xenon.

The dielectric-barrier-discharge also called silent discharge is a discharge between two electrodes with a gas filled gap and an additional dielectric in between the electrodes. This dielectric prevents the discharge from forming a dc-arc in the discharge gap. Typical geometries are parallel plate reactors or coaxial shaped lamps (*Fig. 3*). DBD are driven by alternating high voltages, originally done by a sinusoidal high voltage of several kV.

However, much more effective is the use of high voltage pulses in the kV range as used in Xeradex lamps made by OSRAM. This method of driving DBD yields efficiencies of up to 40%.

The discharge gap is filled with gas at a pressure of 100 – 1000 mbar in the case of 172 nm lamps filled with e.g. xenon. The discharge produces the unstable xenon molecule Xe_2, a so-called excimer, which emits UV light while dissociating.

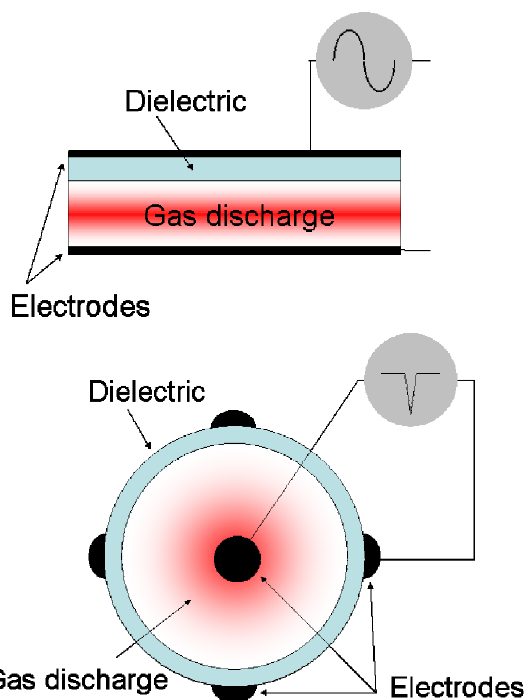

Fig. 4 *Parallel plate or cylindrical shaped DBD (Osram type)*

This process emits radiation of 172 nm with FWHM of 14 nm.

172 nm is the lowest possible wavelength for classical lamps made of quartz tubes. Lamp length and thus treated substrate size of more than 2 m are thus possible.

Basics on 172 nm radiation

The radiation at 172 nm is equivalent to a photon energy of 7.2 eV or 166 kcal/mol and can crack many hydrocarbons (see Fig. 6).

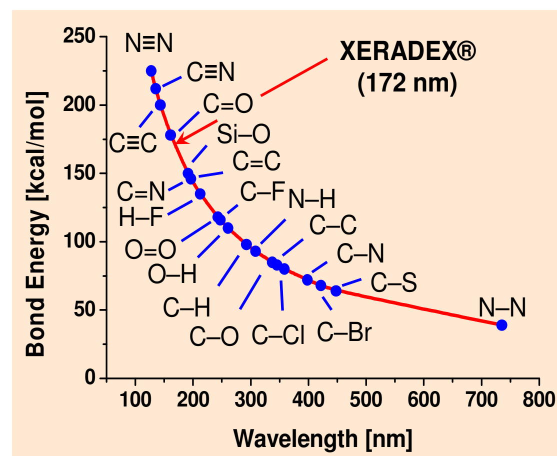

Fig. 5 *Common bond energies compared to the energy of 172 nm photons*

This is the mechanism for the above-mentioned VUV cleaning.

As shown in Fig. 6, 172 nm radiation breaks the O=O bond in oxygen and produces O_3 and single oxygen atoms ($O(^1D)$).

Because 7.2 eV is not enough energy for a dissociation of N_2 the production of NO_x in air is avoided. N_2 is therefore transparent for 172 nm radiation and can be used as cheap working gas to produce an atmosphere for substrate treatment without ozone treatment, radiation treatment of 3-dimensional objects and as purging gas for luminaires.

In contrast to a pure ozone treatment, the radiation energy is directly deposited at the near-surface chemical bonds so that it can accelerate chemical surface processes like oxidation or polymerization.

VUV surface treatment in vacuum or under low pressure conditions

Surface treatment under vacuum could be indicated if the treated surfaces must not be influenced by chemical reactions due to the presence of oxygen, ozone, nitrogen and other gases. Subsequent process steps in vacuum could also make a vacuum treatment preferable to avoid handling in atmosphere, e.g. cleaning prior to coating.

VUV light is the only possibility for cleaning in a vacuum anyhow. If applied, another advantage of 172 nm radiation is utilized. The radiation removes the ubiquitous film of adsorbed water.

Xeradex lamps from OSRAM are available in a vacuum version where the lamp socket has an integrated KF50 flange. The electrical connection to the lamp is completely outside the vacuum so that no further electrical feedthroughs are needed. This is an important advantage because high voltage electrical connections tend to initiate shorts and arcs in low pressure environments if the vacuum conditions are not perfect (or, in other words, if the pressure is near the Paschen Minimum).

Photo assisted CVD is another field of application where a low pressure environment is needed. There is the need for a long free path length of the particles involved in the reactions, which should be of the order of the reactor dimension. In photo-assisted CVD, the VUV light source supplies the energy that is needed to keep the process running. This is similar to the role of the plasma in plasma-enhanced CVD (PECVD), but with the advantage that the surface bombardment with ions, electrons and accelerated neutrals and active species is absent.

In case of PECVD fast ions, accelerated in the plasma sheath, can cause problems especially if the substrate is a semi-conductor material. This physical effect can be diluted by various methods developed over the last 50 years, most of them decreasing the efficiency, but it cannot be avoided totally because the substrate is always a part of the plasma boarder.

New applications for 172 nm radiation

Beside the applications of surface cleaning and activation there are many different applications of VUV radiation that have been developed in the last few years – and it is still an active field of development. The most important are presented here.

Ozone production

As mentioned before, VUV radiation produces ozone from air or pure oxygen. With an efficiency of 82(92) g/kWh in air (oxygen) VUV radiation is a very efficient method of producing ozone[1]. No NO_x is produced in air because the photon energy of 7.2 eV is slightly too low to dissociate N_2.

Especially if high amounts of ozone are needed, strongly localized or without any warm-up time or without NO_x generation, Xeradex VUV lamps are the method of choice.

Photo-assisted rapid oxidizing for producing SiO_2 and other oxides

Although ozone has with E = 2.07 eV the second highest oxidation potential after

[1] In-house tests at OSRAM GmbH

fluorine, the combination of radiation and ozone is by far more effective. While ozone and the O(^{1}D)-radical are delivering the reactive species, every 172 nm photon delivers an additional 7.2 eV of energy to crack bonds of the solid state lattice. The effects are not only added together but they potentiate each other.

This interaction of both effects is called photo-assisted rapid oxidizing. One of the most interesting materials for a controlled oxidation is silicone, because silicone oxide films are a part of nearly all semiconductor components. And they have to be produced both quickly and of high and reproducible quality.

The standard method to oxidize silicone is to heat it up to between 800°C and 1200°C in wet or dry atmosphere for hours[2]. This leads to SiO_2 films of high electrical quality and high density. Photo-assisted oxidation can take place at much lower temperatures, but nevertheless yield oxide films below 10 nm of the highest quality.

H. Oyanagi and A. Fukano found that with VUV photo-oxidation the same or higher densities can be achieved compared to the classical method of thermal oxidizing.

Material	Density (g/cm^3)
VUV(172nm) oxidized Si	2.27
thermal dry oxidized Si	2.24
thermal wet oxidized Si	2.20
cristobalite	2.32

Table 1[3] *Density of SiO_2 generated with different methods*

Various CVD and PECVD methods can take place at high temperatures of several hundred °C but yield SiO_2 with hydrogen content of 1-10%[4]. Beside these thin film technologies, photo-oxidation can also be useful for thick film applications. Nakata et al.[5] recognized that a stack of thin film photo-oxidized SiO_2 and low temperature PECVD SiO_2 have better characteristics than a high-temperature annealed PECVD film of double the film thickness.

Besides producing SiO_2, photo-assisted rapid oxidizing is also possible with many other oxidizable materials e.g. germanium.

Photo CVD and photo decomposition

As the energy of 7.2 eV is enough to crack various bonds, VUV radiation can be used as the energy source for chemical vapor deposition. Especially in the microelectronics industry, the advantages of this method are the low process temperature and the complete absence of charged particles.

Thick dielectric films can be produced this way. It has been shown that with this method SiO_2, SiN, SiN_xO_y and Ta_2O_5 films can be generated at low temperatures as low as 300°C from precursors like Silane etc.[2] with high rates of 500Å/min.

Beside these low pressure gas phase reactions, thin films that have been coated from a liquid solution can also be converted into stable films or metal at atmospheric pressure.

Low-k films like polyimide and porous SiO_2 can be made this way. Polyimide[6] can be made from polyamic-acid and SiO_2 from a TEOS-solution[2].

Metal, mainly as an activator for electroless plating, can be made by photo decomposition of metalorganic films. With 172 nm VUV radiation Cu[2] and Pd[7] were made, but many other materials like Pt or Al_2O_3 are possible[2].

[2] Boyd, Zhang, Kogelschatz in "Photo-Excited Processes, Diagnostics and Applications", Aaron Peled (ed.), 161-199, 2003 Kluwer Academic Publishers

[3] A.Fukano, H.Oyanagi; Highly insulating ultrathin SiO2 grown by photooxidation"; Journal of Applied Physics; Vol. 94 No. 5; 1.Sep.2003

[4] Handbook of thin film deposition; Krishna Seshan (ed.) 2nd edition 2002; Noyes Publication; p.138

[5] Nakata, Okamoto, Hamada, Hoga, Ishii; Asia display / IDW'01, Proc.of the 21st Internat Display Res.Conf. Vol.1 Oct 16-19, 2001

[6] Zhang, Boyd; Optical Materials(1998) Vol. 9 issue 1-4 p. 251-254

[7] Zhang, Boyd; Thin Solid Films(1998) Vol. 318 issue 1-2 p. 234-238

Annealing and post-polymerization

Annealing is a process that increases a special material property mostly by high temperature baking or plasma treatment in an already produced film. However, material films can also be annealed by VUV radiation. It has been shown, for instance, that Ta_2O_5 films can be annealed by 172 nm radiation at relatively low temperature[2]. The film thickness that can be treated depends on the transparency for 172 nm radiation. This thickness is in most cases much higher than for plasma treatment.

A similar process that has nothing to do with microelectronics is the improvement of silicon-based barrier coatings on polymer foils. The photon energy is used to build up a strong network inside a SiO_x film made from polysilazane lacquer[8]. The advantage of the use of VUV radiation in this case is the film formation at low temperature and at normal pressure on big surfaces up to 2 m in width. The penetration depth for VUV radiation makes it possible to produce films of 0.1 µm thickness.

Polymerization and surface shaping

As opposed to the above-mentioned SiO_x films, 172 nm radiation can also be used to directly start polymerization in lacquer systems.

Some work is done in the development of photoinitiator-free acrylate lacquers and silicone-based coatings[9], which can be polymerized completely with 172 nm radiation. The film thickness is limited by the penetration depth for this special wavelength.

For another application this limited depth is used to structure the surface of a coating. Most lacquers have shrinkage while polymerizing. If the radiation does not penetrate the wet lacquer film to the substrate surface, the polymerizing top part of the wet film can form a short scale structure (*Fig. 7*) while shrinking. A complete hardening of the film with UV of longer wavelength or e-beam will freeze this structure. With this method lacquers can be matted without any additives[10].

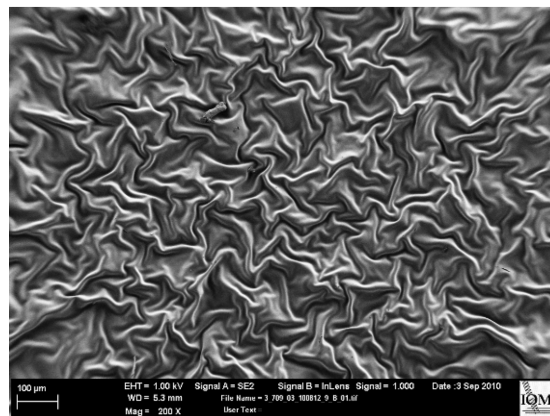

Fig. 8 *Lacquer film structured by VUV radiation to get matt surface finish (SEM picture by IOM Leipzig)*

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[8] L. Prager et al. ; Chem. Eur. J. 13 (2007) 8522-8529

[9] Doelle et al., Langmuir, 2009, Vol. 25, no. 12, pp. 7129-7134

[10] Bauer, F.; Decker, U.; Czihal, K.; Mehnert, R.; Ried ... , Progress in Organic Coatings. An International Journal (2009) Vol.64, No.4, p.474-481.