UDK621.3:(53+54+621+66), ISSN0352-9045

REACTIVE PLASMA TECHNOLOGIES IN ELECTRONIC INDUSTRY

Miran Mozetič

Plasma laboratory, Institute of Surface Engineering and Optoelectronics,
Ljubljana, Slovenia

INVITED PAPER
MIDEM 2003 CONFERENCE
01. 10. 03 - 03. 10. 03, Grad Ptuj

Abstract: Application of novel materials, higher standards and demands for environment protection have lead to introduction of novel advanced methods for materials processing. Most of them are dry and run under heavily non-equilibrium conditions. A mixture of gas is transformed into the state of plasma. Molecules are excited, dissociated and ionized and the resultant radicals are used to treat electronic components. Examples of technologies include chemical plasma cleaning, plasma activation, selective plasma etching and plasma ashing. Chemical plasma cleaning has been introduced in microelectronics as an alternative to physical plasma cleaning, whose drawback is a re-deposition of sputtered material. In classical electronic industry, the chemical plasma cleaning has been introduced as an environmentally benign alternative to wet chemical cleaning. Plasma activation has become the most efficient method for a dramatic increase of the polymers wettability and thus affinity to metallization. Selective plasma etching is an excellent method for treatment of polymer-matrix composites prior to metallization, while plasma ashing is a simple and reliable method for organic dust removal.

Some examples of industrial application of above technologies will be presented. Advantages as well as drawbacks and limitations of the technologies will be discussed.

Reaktivne plazemske tehnologije v elektronski industriji

Izvleček: Uporaba novih materialov, višjih standardov in zahtev po zaščiti okolja so vodili k vpeljavi naprednih postopkov obdelave materialov. Večina sodobnih postopkov je suhih in potekajo pri termodinamsko močno neravnovesnih razmerah. Mešanico plinov pretvorimo v stanje plazme. Plinske molekule se v plazmi vzbudijo, disociirajo in ionizirajo, tako nastale radikale pa uporabimo za obdelavo elektronskih komponent. Primeri tehnoloških postopkov, ki temeljijo na uporabi reaktivne plazme, so kemijsko plazemsko čiščenje, plazemska aktivacija, selektivno plazemsko jedkanje in plazemsko upepeljevanje. Kemijsko plazemsko čiščenje so najprej uporabili v mikroelektroniki kot alternativo fizikalnemu plazemskemu čiščenju, katerega pomanjkljivost je nalaganje razpršenega materiala na površine. V klasični elektronski industriji se kemijsko plazemsko čiščenje počasi uveljavlja kot okolju prijazen nadomestek mokrega kemijskega čiščenja. Plazemska aktivacija je postala najuspešnejša metoda za povečanje omočljivosti polimerov, ki je potrebna za učinkovito metalizacijo plastičnih komponent. Selektivno plazemsko jedkanje je odlična metoda za obdelavo kompozitnih materialov s polimerno matriko, medtem ko je plazemsko upepeljevanje preprosta in zanesljiva metoda za odstranjevanje organskih prašnih delcev z različnih površin. V prispevku je opisana uporaba nekaterih plazemskih postopkov za industrijsko uporabo in prednosti, pomanjkljivosti in omejitve navedenih tehnologij.

1. Introduction

The very traditional trend in electronic industry is miniaturization. Since the beginning of a massive production of microelectronic devices the miniaturization demands required application of novel, by that times unknown technologies. Wet chemical etching has been replaced with advanced dry etching processes such as ion beam etching, reactive ion etching and plasma stripping. Wet chemical deposition methods as well as thermal evaporation have been replaced by a variety of plasma- or ion beam- assisted deposition methods currently often referred as physical (PVD) or chemical (CVD) vapor deposition techniques. Traditional cleaning methods have been replaced with novel plasma based cleaning techniques. More recently, further miniaturization is expected in three-dimensional devices based on novel nano-scale materials.

Classical electronic industry is also undergoing miniatuarization trends. Unlike microelectronic industry where the materials expenses plays a minor role, a driving force of miniaturization of classical electronic devices is the cost of materials. Currently, the classical materials such as metals, polymers and ceramics are being gradually replaced with composites. Promising substitutes for metals are graphite-polymer composites and glassy carbon, while ceramics are replaced with ceramic composites. A major advantage of a carbon-based composite over a metal is a low weight, good mechanical properties and excellent chemical resistance.

A major consideration in both classical electronics and microelectronics is environment. The environment protection laws became severe and the general expectation is even tightening the restrictions. Nowadays any technological effort takes into account the ecological suitability of the materials processing.

2. Reactive plasma

The problems of miniaturization, application of novel materials and environment protection have been solved with application of technologies that are based on application of low-pressure plasmas. Namely, traditional methods were found inadequate to solve novel demands. Traditional methods are based on thermodynamically equilibrium processing techniques. Wet chemical treatments as well as thermal deposition techniques are good examples. The driving force in all these techniques is temperature. The reactivity of particles involved in these techniques depends on temperature. Since many advanced materials do not stand high temperature processing the application of traditional techniques is obviously limited. The only solution to current demands is therefore application of a heavily non-equilibrium media for materials processing.

One of the best examples of non-equilibrium medium is low-pressure plasma. Plasma is sometimes referred as the fourth state of the matter - solid, liquid and gaseous being the first three. It is created in a gas under low pressure when electric current is allowed to pass through. This can be achieved in a variety of gaseous discharges including the DC, RF and MW discharge. In any case, the free electrons are accelerated in an electric field. When they gain enough energy (above the ionization threshold) the electrons can ionize neutral molecules. As more electrons are generated at ionization collisions the number of electrons in the gas increases and finally reach such a large value that the gas becomes conductive and the discharge self-sustained. A simultaneous effect of electron multiplication is a formation of positive ions. The density of positive ions in plasma is often equal to the electron density.

Energetic electrons in plasma are not only capable of ionizing molecules, but they can also suffer other types of inelastic collisions with neutral molecules. The diatomic gaseous molecules can be dissociated, excited in a variety of states including rotational, vibrational and electronic states, and the atoms can be excited in electronic states as well. Plasma therefore consist a variety of particles that are present in a normal gas only in low quantities, such as neutral atoms and highly excited molecules. Since the radiative life time of many states in long (some states are metastable) the particles may be found in extremely high states - in nitrogen plasma, for instance, the average vibrational state is easily about 20 corresponding to the internal vibrational temperature well over 10.000°C. Similarly, the neutral atom density may be also high and the dissociation degree may approach unity, otherwise typical for temperature of 50.000°C.

On the other hand, the kinetic temperature (i.e. average kinetic energy) of gaseous particles often remains close to room temperature. The discrepancy between the internal and the kinetic gas temperature is due to a poor kinetic interaction of energetic electrons with heavy particles (molecules and atoms). At an elastic collision only a fraction (often less than 0.001) of an electron kinetic energy can be transferred to a heavy particle. The kinetic temperature of heavy particles is therefore not much influenced by the electron energy. As long as one can avoid direct heating of heavy particles in electric field and some other effects including superelastic collisions between vibrationally excited molecules and atoms, the kinetic temperature of heavy particles remain low. These conditions, i.e. a high concentration of excited particles at low kinetic temperature, are ideal for advanced treatments of materials in electronic industry. Several technologies based on application of such plasmas have been developed and some are described below.

3. Discharge cleaning

Discharge cleaning (often called plasma cleaning) has been first introduced in microelectronics where the demands of materials cleanliness were the highest. Later, it has been introduced to other industrial branches, and the main reason was a requirement of ecological friendly processing. Discharge cleaning is an ecological benign substitute of wet chemical cleaning. The wet chemical cleaning produces large quantities of used chemicals that pollute environment. Plasma cleaning, on the other hand, produces little, if any, pollutants. Organic impurities are often removed with oxygen plasma, while oxidizing impurities (O, Cl, S) are effectively removed with hydrogen plasma.

Hydrogen plasma has been successfully applied for cleaning silver contacts in switching devices. The major reason for introducing plasma cleaning was ecological - contacts were previously cleaned with freon that has been forbidden due to harmful effects to ozone layer in the upper atmosphere. Figure 1(a) is a typical AES depth profile of a contact as received from a production line. There are several impurities on the surface including organic impurities as well as oxygen, sulfur, chlorine and potassium. The contaminants are effectively removed by hydrogen plasma treatment. A typical treatment time is 1 minute thus suitable for massive industrial production. The AES depth profile after plasma treatment is shown in Figure 1(b). There are hardly any impurities on the surface except of traces of O and S probably due to secondary pollution since samples were exposed to air prior to AES analyses. The effect of perfect surface cleanliness is demonstrated in Figure 1(c) that is a plot of contact resistance of the switching device after plasma cleaning. The contact resistance remains extremely low even at poor contact force.

Copper components heavily contaminated with organic impurities are best cleaned with oxygen plasma followed by a hydrogen plasma treatment. Namely, hydrogen plasma is not most efficient in removing organic compounds. Oxygen plasma treatment is more efficient, but a drawback of oxygen plasma treatment is often a formation of a thin oxide film on the material surface. This oxide film is effectively reduced with hydrogen plasma. Figure 2 demonstrates the efficiency of combined oxygen/hydrogen plasma cleaning. The sample as received from a production line is covered with a variety of impurities, organic compounds being predominated. Chemical treatment reduces amount of impurities substantially but not all. Oxygen plasma treatment effectively removes organic compounds but oxidizes the material. Finally, hydrogen plasma treatment reduces the oxide film leaving the surface virtually atomically clean.

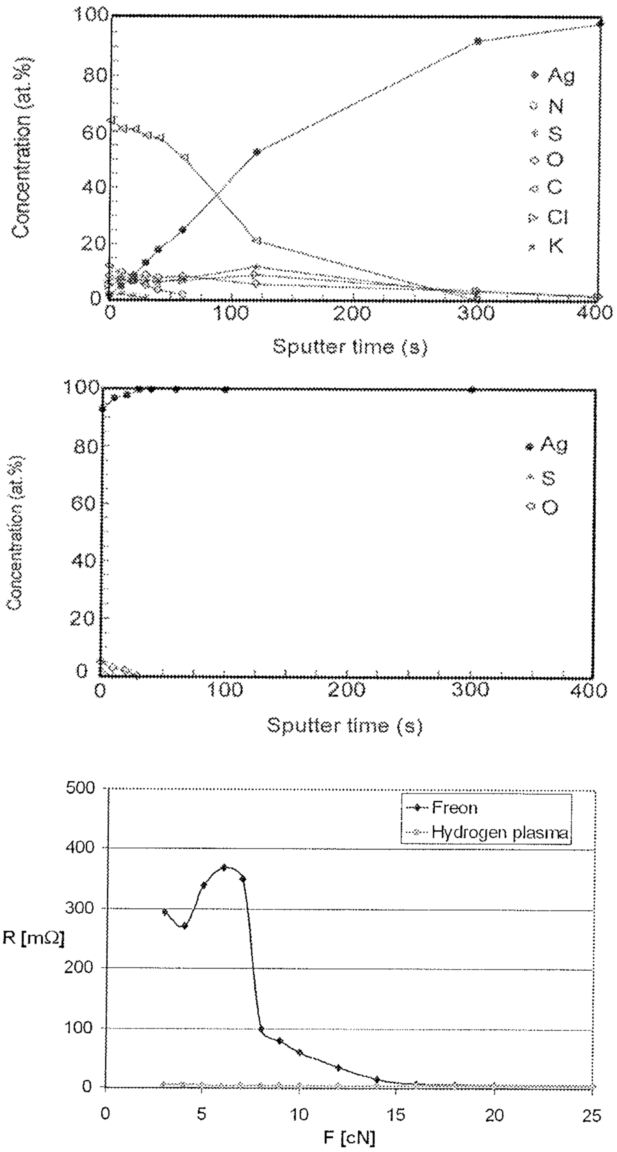
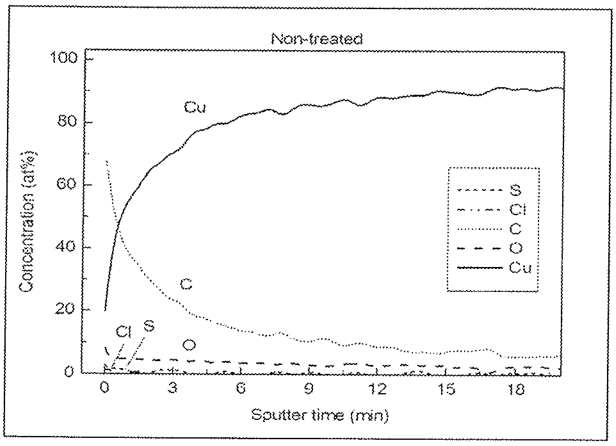


Figure 1. *AES depth profile of a silver contact from a switching device as received (a) and after hydrogen plasma cleaning (b). The contact resistance between the contacts of a plasma cleaned switch compared to conventional freon-cleaned switch (c).*



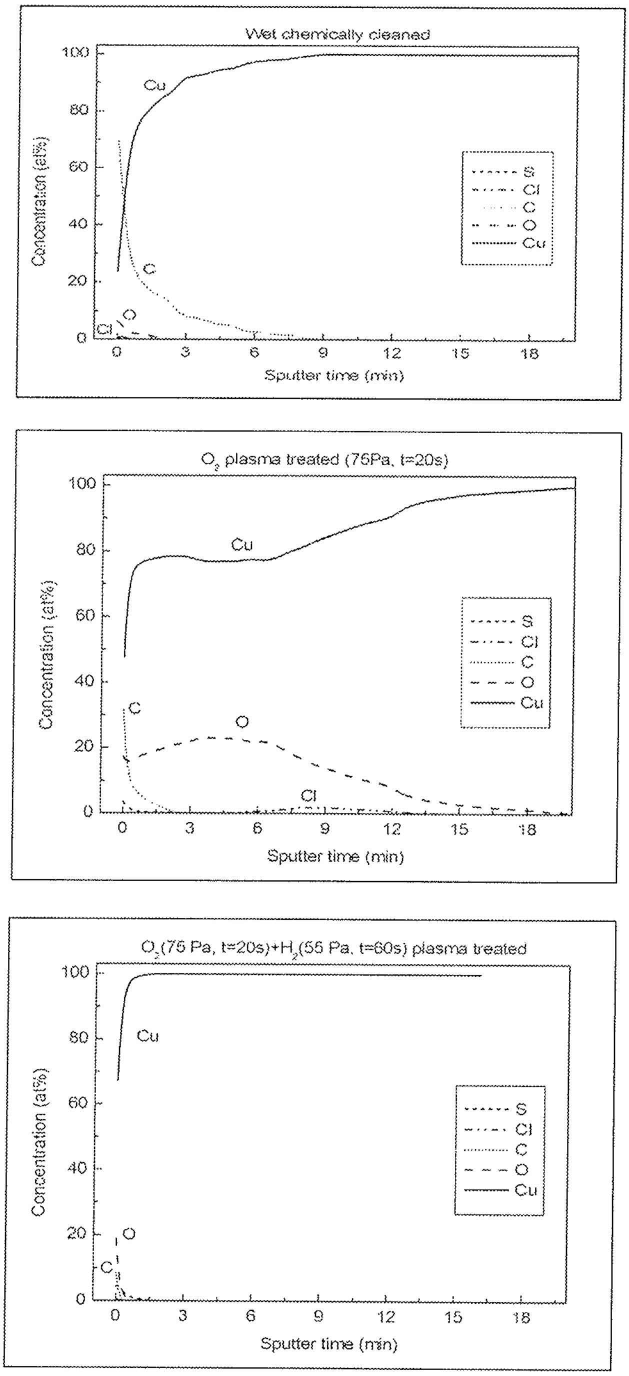


Figure 2. *AES depth profiles of a copper component: as received from production line, wet chemically cleaned, oxygen plasma cleaned and hydrogen plasma cleaned.*

4. Surface activation

Polymers are often made from unpolar groups resulting in a poor surface wettability. In order to increase the wettability prior to painting, printing or metallization, the surface should be activated. Surface activation is performed by a variety of techniques including the wet chemical treatment, UV irradiation, ion beam treatment, laser modification and mechanical roughening, but the best method proved to be low-pressure oxygen plasma oxidation. By plasma treatment the surface become rich with polar groups enhancing the surface wettability dramatically. Figure 3 represents a water drop on a housing of a capacitor prior and after plasma activation. The difference in surface wettability is clear. Even more important is the fact that optimal surface wettability is obtained after less that 0.1 s of plasma treatment - a fact that makes plasma activation extremely suitable for a massive industrial production. Figure 4 presents a contact angle of a water drop on a polymer foil. As expected the contact angle decreases dramatically in first few seconds of plasma treatment, but tends to increase slowly with further plasma action indicating the overestimation of plasma treatment should be avoided.

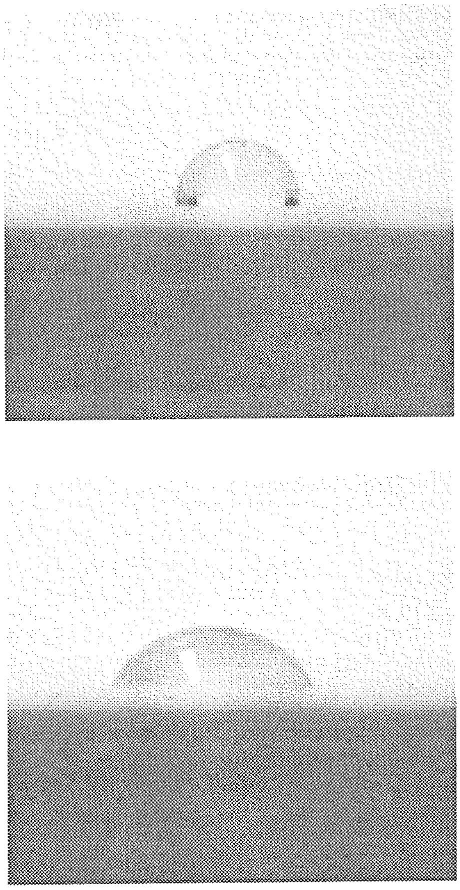


Figure 3. *A water drop on a capacitor housing before (left) and after (right) plasma treatment*

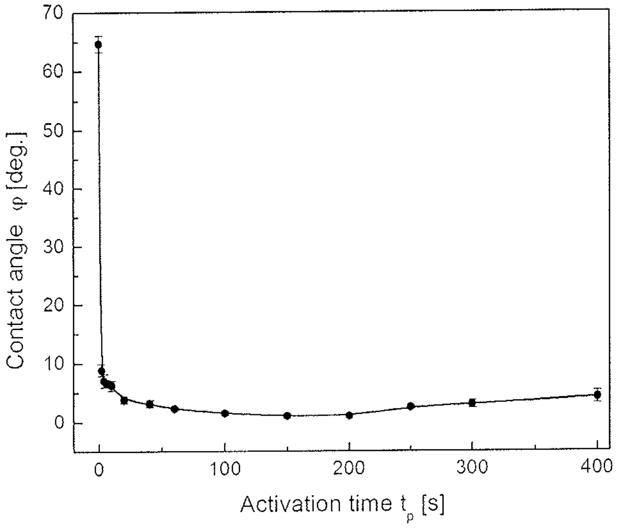


Figure 4. *A contact angle of a water drop on a polymer foil*

5. Selective plasma etching

Metals are being gradually replaced with polymer matrix composites. The major advantage of a graphite-polymer composite over a metal is a low weight, good mechanical properties and excellent chemical resistance. A major drawback, on the other side, is a poor affinity to metallization. A traditional method of polymer-matrix composite metallization is surface activation with palladium followed with a chemical metallization. An excellent substitute for those ecological unsuitable technologies is plasma treatment. Unlike the upper methods that produce environmentally harmful residues, plasma treatment is an ecologically benign technology. The plasma treatment effects are threefold: first, increases the surface wettability (Figure 5), second, it reducer the concentration of polymer on the surface (Figure 6), and third, it makes the surface rough enough to assure good adhesion between the substrate and the metallization (Figure 7,8).

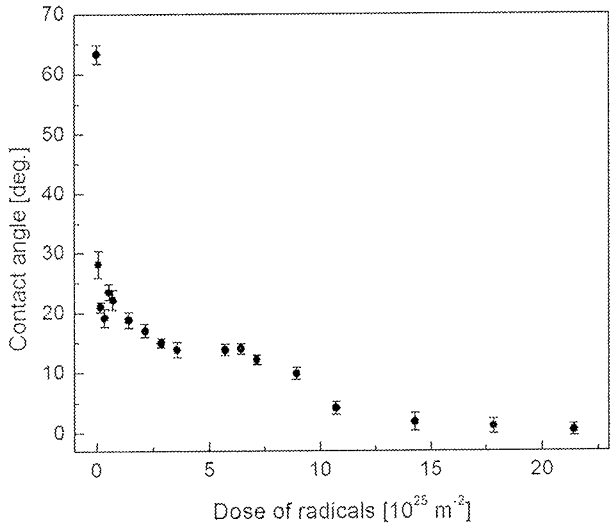


Figure 5. *Contact angle of a water drop on a graphite-polymer surface versus the dose of oxygen radicals*

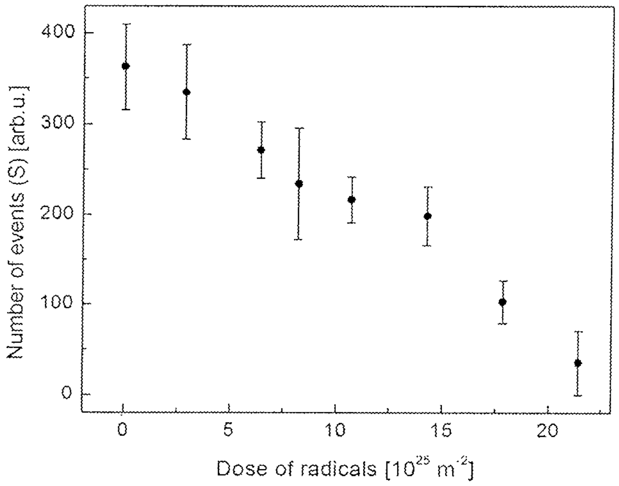


Figure 6. *Concentration of sulfur in the surface layer of a graphite-pps polymer composite versus the dose of oxygen radicals.*

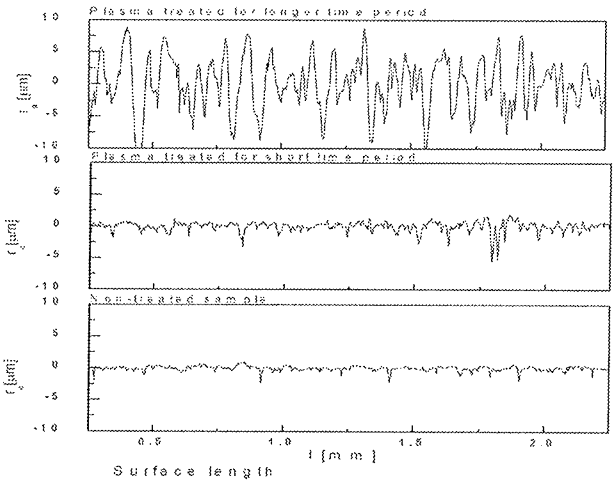


Figure 7. *Evolution of a surface roughness of a graphite-pps polymer composite during plasma treatment.*

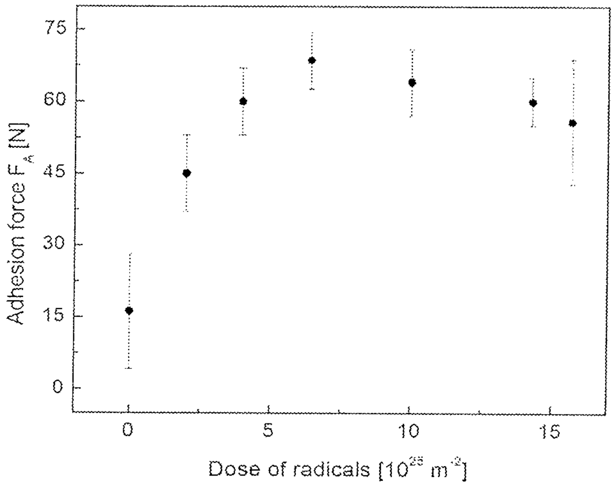


Figure 8. *Adhesion force of a metallization layer on a graphite polymer-matrix composite.*

The selective plasma etching technology is also an excellent method for treatment of a variety of polymer matrix composites to reveal the distribution and orientation of different particles in the matrix. It is the unique method to determine the composition of different films and paints. Figure 9(a,b,c) represent scanning electron images of a photographic film during plasma etching. Untreated samples reveal no significant structure. A 30s plasma treatment reveals spherical holes indicating the presence of gaseous bubbles in the uppermost layer of a photographic film. The grains of silver halide are observed only after prolonged plasma treatment.

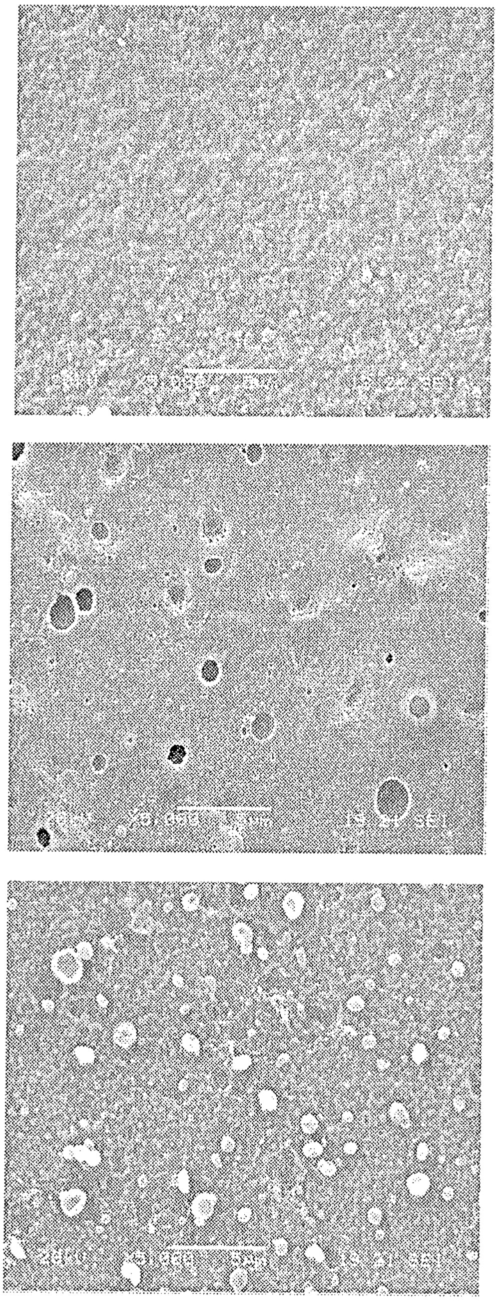


Figure 9. *SEM images of a photographic film before plasma treatment (upper), after a short plasma treatment (middle) and prolonged (lower) treatment*

Another example of application of the selective plasma technology is an advanced paint for automotive industry. Figure 10 represents a SEM image of the paint before and after plasma treatment. It is clear that plasma treatment clearly reveals the original distribution of mica flakes in the coating.

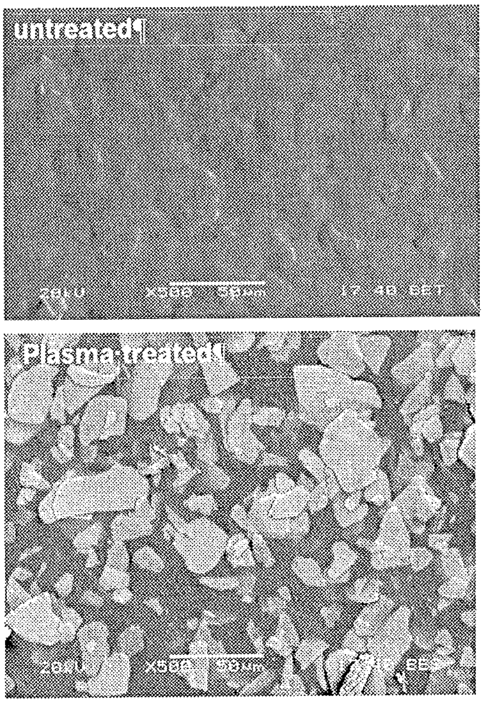


Figure 10. A SEM image of a mica paint before and after oxygen plasma treatment

6. Conclusions

In the past few years the reactive plasma technologies have been successfully applied to modern electronic industry. Apart from the technical advantages, the major reason for introduction plasma based technology is environment protection. The reactive plasma technologies are usually ecological benign alternatives to wet chemical treatments. The maintenance as well as consumables costs are often much lower than corresponding costs of traditional techniques. The major drawback of novel technologies, however, is a high cost of plasma reactors. It is expected that these expenses will decrease in the next future, as more users of reactors will appear in the market.

References

/1/ B. Chapman, Glow Discharge Processes (Willey, New York, 1980).

/2/ H. Boeing, Plasma Science and technology (Cornell Univerity Press, London, 1982).

/3/ M. R. Wertheimer, L. Martinu and E. M. Liston, Plasma sources for polymer surface treatment, Handbook of thin film Process Technology, ed. by D.A.Glocker and S.I. Shah. Bristol (Inst. Of Physics Publishing, Bristol, 1998).

/4/ A. Ricard , Reactive plasmas (Societe Francaise du Vide, Paris, 1996).

/5/ I. Šorli, W. Pettasch, B. Kegel, H. Schmidt and G. Liebel, Inform. Midem 26, 35 (1996).

/6/ I. Sorli and R. J. Rocak, Vac. Sci. Technol. A18, 338 (2000).

/7/ Babič, D., Poberaj, I., Mozetič, M., Rev. Sci. Instr. 72, 4110 (2001).

/8/ Poberaj, I., Babič, D., Mozetič, M., J. Vac. Sci. Technol. A20, 189 (2002).

/9/ Mozetic, M., Ricard, A., Babic, D., Poberaj, I., Levaton, J., Monna, V., Cvelbar, U., J. Vac. Sci. Technol. A21, 369 (2003).

/10/ Wise, H., Wood, B.J., Gas and Surface Reaction Collisions, Advances in Atomic and Molecular Chemistry, ed. D.R. Bates, I. Estermann, Academic Press, New York (1967).

/11/ M. Mozetič and A. Zalar, Appl. Surf. Sci. 158, 263 (2000).

/12/ P. Pelicon, M. Klanjšek-Gunde, M. Kunaver, J. Simčič and M. Budnar, Nucl. Instrum. Meth. 190, 370 (2002).

/13/ M. Klanjšek-Gunde and M. Kunaver, Appl. Spectrosc. 57, 1266 (2003).

/14/ M. Kunaver, M. Klanjšek - Gunde, M. Mozetič and A. Horvat, Surf. Coat. Inter. B 86, 175 (2003).

/15/ S. Gomez, P. G. Steen and W. G. Graham, Appl. Phys. Lett 81, 19 (2002).

/16/ H. Singh, J. W. Coburn and D. B. Grawes, J. Appl. Phys 88, 3748 (2000).

/17/ D. J. Wilson, N. P. Rhodes and R. L. Williams, Biomaterials 24, 5069 (2003).

/18/ Z. Y. Wu, N. Xanthopoulos, F. Reymond, J. S. Rossier and H. H. Girault, Electrophoresis 23, 782 (2002).

Miran Mozetič
Plasma laboratory,
Institute of Surface Engineering and Optoelectronics,
Teslova 30, 1000 Ljubljana, Slovenia

Prispelo (Arrived): 15.09.2003 Sprejeto (Accepted): 03.10.2003