

REMOVAL OF A THIN HYDROGENATED CARBON FILM BY OXYGEN PLASMA TREATMENT

ODSTRANJEVANJE TANKE PLASTI HIDROGENIRANEGA OGLJIKA S KISIKOVO PLAZMO

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Capability of low pressure oxygen as a medium for removal of hydrogenated carbon thin films is demonstrated. The film was deposited onto polished iron discs by CVD method. Discs were mounted into a discharge chamber which was evacuated to the ultimate pressure of about 5 Pa. Methane of commercial purity was leaked into the chamber during continuous pumping so the pressure of 100 Pa was established. Weakly ionized plasma was then created in the chamber by an inductively coupled RF generator operating at the frequency of 27.12 MHz and the power of about 200 W. The methane molecules dissociated in the plasma forming CH_3 radicals that adsorbed on the sample surface causing formation of a thin film of hydrogenated carbon. AES depth profiling showed that a 3 nm thick film was formed after 200 s of plasma treatment. Samples were then exposed to oxygen plasma in the same chamber, and characterized by AES as well as water drop contact angle. After 12 s of oxygen plasma treatment the samples were visually free of carbon and the AES depth profiling proved it. The contact angle of a water drop decreased from initial 80° to about 10° indicating a rapid transformation of the surface properties from hydrophobic to hydrophilic character. The experiments allowed for estimation of the cleaning efficiency which was about 0.25 nm/s.

Keywords: hydrogenated carbon, gaseous plasma, methane, oxygen, Auger electron spectroscopy, hydrophilic

Prispevek opisuje možnosti, ki jih daje kisikova plazma pri odstranjevanju tankih plasti hidrogeniranega ogljika. Plasti so bile pripravljene na železnih poliranih vzorcih z nanosom iz parne faze. Vzorci so bili postavljeni v razelektritveno posodo vakuumskega sistema. Sistem je bil najprej izčrpan do končnega tlaka okoli 5 Pa, potem pa smo ob stalnem črpanju dovajali metan pri tlaku 100 Pa. V metanu smo ustvarili plinsko plazmo z razelektritvijo, ki smo jo vzbujali z radiofrekvenčnim generatorjem moči okoli 200 W in frekvence 27,12 MHz. Molekule metana v plazmi disociirajo, nastali radikali CH_3 pa se lahko vežejo na površino vzorca in počasi tvorijo tanko plast hidrogeniranega ogljika. Profilna analiza s spektroskopijo Augerjevih elektronov (AES) je pokazala, da je po 200 s obdelave nastala plast debeline okoli 3 nm. Vzorci so bili potem izpostavljeni delovanju kisikove plazme v istem reaktorju. Po izpostavitvi so bili analizirani z AES, izmerili pa smo tudi kontaktne kote vodnih kapljic v odvisnosti od časa izpostavitve kisikovi plazmi. Globinski profili AES so pokazali izredno veliko stopnjo čistosti vzorcev po okoli 12-sekundni obdelavi. Kontaktni kot vodne kapljice je bil sprva 80° , kar kaže na hidrofobnost plasti hidrogeniranega ogljika. Že po 1 s obdelave s kisikovo plazmo pa se je zmanjšal na okoli 10° , kar kaže na hitro funkcionalizacijo s polarnimi skupinami. Rezultati raziskav so omogočili izračun hitrosti jedkanja, ki je za navedene vzorce okoli 0,25 nm/s.

Ključne besede: hidrogenirani ogljik, plinska plazma, metan, kisik, spektroskopija Augerjevih elektronov, hidrofilizacija

1 INTRODUCTION

Energy supply is a major global consideration of future generations. Currently, the majority of energy is supplied by burning fossil fuels. The problem of this energy source is not only that it will be exhausted sooner or later, but the burning also causes release of huge quantities of greenhouse gases, such as CO_2 , which contributes to the heating of Earth's atmosphere. Moreover, as recent history shows, the availability of energy sources is often subject to local political situation. The future energy sources should therefore be both friendly to the environment and independent from local political situation. While many methods for energy production have been invented, none of them is effective enough to be a suitable replacement of carbon fuels as the consumption of energy is expected to grow continuously due to the expected growth of population as well as higher consumption per capita in third world countries.

The most natural solution of the problem is usage of energy arising from our Sun. The Sun is a rather young star and is expected to supply energy for the next billion years. The temperature on the Sun surface is close to 6 000 K so it radiates energy as a black body covering a broad range from IR to UV part of the spectrum. The majority of energy reaching the Earth is in the visible range, i. e. photons of the energy of few eV. The Earth receives the energy flux of close to 1000 W/m^2 . Taking into account the Earth diameter which is about 12 700 km one can calculate the power reaching the earth

$$P = \frac{1}{4} \pi d^2 E_0 = 4 \times 10^{17} \text{ W} \quad (1)$$

Here d is the Earth's diameter and E_0 the flux of energy from the Sun at the Earth distance (close to 1000 W/m^2). The current needs of all population are approximately $3 \times 10^{10} \text{ W}$ so the energy coming from the Sun is 10 million times the needs of the population. The humans therefore use only a negligible fraction of available energy.

The problem arises from the fact that the energy in the form of visible light photons does not cover all of humanity's energy needs. Beside visible light, we need other forms of energy, such as electricity. Not surprisingly, efforts have been made worldwide to develop methods for conversion energy from visible light photons to electricity. Solar panels have been developed decades ago and are currently being used, but only a small fraction of the globally consumed energy comes from this source. There are several reasons that prevent general adoption of solar cells including geographic (climate) reasons, high investment costs, rather poor efficiency, and aging effects. Also, it seems that contamination of the panel surface by dust is far from a minor problem, especially in the deserts where other conditions are favorable. Although recent results in development of new generation of solar cells with quantum dots or nanowires¹⁻⁵ are promising, their application is still questionable.

The original source of energy from our Sun are not photons of visible light. Sun makes energy from nuclear fusion (reactions between hydrogen isotopes). Huge amount of energy is released by fusion. At the reaction



an amount of energy equal to almost 18 MeV is released. The majority of energy (more than 14 MeV) is taken by the neutron in terms of its kinetic energy, and the rest is taken by the He nucleus, also in terms of the kinetic energy. This reaction is really energetic: 1 kg of fuel (hydrogen isotopes) produces about $100 \cdot 10^6$ kW h of energy. A kilogram of coal, on the other hand, gives only about 5 kW h – 8 orders of magnitude less energy.

Nuclear fusion is possible only at extremely high temperatures, because a substantial amount of energy (0.4 MeV) has to be invested in the pair of nuclei in order to overcome the electrostatic energy barrier. Such high temperature is not available at the sun surface, but only in the Sun core. The temperature in the Sun centre is estimated to $15 \cdot 10^6$ K. This is obviously enough for fusion reactions heating our Sun. Extremely fast neutrons and helium nuclei formed at fusion reactions collide with other nuclei and are thermalized (achieve Maxwell – Boltzmann kinetic energy distribution function) so they cannot reach the Sun surface. Strong convection allows for transfer of energy from the Sun core toward the surface. Adiabatic cooling occurs on the way so the Sun crust is not as hot as the core. Finally, the Sun surface emits photons according to the Stefan – Boltzmann law and what we get at the Earth surface is a flux of mostly visible light photons at the value close to 1000 W/m^2 .

Since the early 1940s, scientists began experimenting with nuclear fusion on Earth, as the energetic neutrons produced in the reaction are more promising particles for energy production than the photons of visible light. Recent results are encouraging so the international community is making many efforts to bring the idea of

having a small Sun here on Earth into fruition. Extremely high temperatures that should be achieved in human-made fusion devices bring many technical problems; a major one is deposition of hydrogenated carbon layers in experimental fusion devices. They are formed when protective graphite coatings, needed due to extremely high temperatures, are eroded by hydrogen atoms. Several research groups worldwide are therefore involved in development of methods for removal of the deposits.

An original approach for removal of hydrogenated carbon deposits is application of thermodynamically non-equilibrium gases, especially oxygen. Such a state of oxygen is obtained by passing molecular gas through a gaseous discharge⁶⁻¹¹. Oxygen molecules in the discharge are partly ionized, dissociated and excited, and the resultant particles are chemically very reactive¹¹⁻¹⁶. A unique property of such particles is that they are very selective – they do interact with certain polymers even at room temperature, but the interaction with graphite is poor¹⁷⁻²³. Exposure of fusion reactors to such oxygen particles would therefore lead to removal of hydrogenated carbon deposits while leaving the massive graphite blocks of protective coatings in fusion reactors rather intact.

Although it is well known that oxygen particles interact chemically with hydrocarbons including polymers²⁴⁻³⁰, very little work has been performed on quantification of results for hydrogenated carbon deposits prepared by plasma deposition. The present paper reports recent results on this phenomenon.

2 EXPERIMENTAL

Experiments were performed in a plasma reactor explained to details elsewhere³⁰⁻³⁴. The reactor is made from glass in order to prevent heterogeneous surface recombination of neutral oxygen atoms so a rather high dissociation fraction is obtained already at a rather low power. The dissociation fraction of 10 % is typical³⁵⁻³⁹. The original experimental setup was modified for current experiments. Two different gases were leaked into the system – methane and oxygen. Methane was used to deposit a thin film of hydrogenated carbon, and oxygen for its removal.

Samples were iron discs with a diameter of 10 mm and a thickness of 0.5 mm. The discs were polished and cleaned by chemical methods. The appearance of hydrogenated film during treatment with methane plasma was observed by a naked eye, but some quantification was performed by Auger Electron Spectroscopy (AES) depth profiling. A classical AES device with a rather poor lateral resolution was applied. The primary electron beam has the diameter of about 40 μm . The samples were sputtered by argon ions in order to measure the depth profiles. The ions had the kinetic energy of 3 keV and were rastered over the surface area of about 5 mm x

5 mm. The sputtering rate for hydrogenated carbon deposits was estimated previously using standard samples and the value was about 2 nm/min.

Water drop contact angle measurements were used in order to determine the surface conditions. A home-made device comprising a CCD camera and a computer with appropriate software was used to measure contact angles of a drop of distilled water with the volume of 3 μL .

3 RESULTS

The discharge chamber was first cleaned by a brief exposure to oxygen plasma, then evacuated to ultimate pressure of about 5 Pa. Methane was leaked continuously during pumping so a stable working pressure of 100 Pa was obtained. Samples were exposed to methane plasma for 200 s and removed from the discharge system. A typical AES depth profile of a sample is presented in **Figure 1**. Samples were then mounted back into the system individually. Oxygen plasma was used to remove the hydrogenated carbon deposits. Samples were visually clean after about 10 s of treatment with oxygen plasma. A depth profile of a sample treated for 12 s is presented in **Figure 2**. Many samples were exposed to plasma for different periods. These samples were characterized by the water drop contact angle method. The contact angle versus plasma treatment time is presented in **Figure 3**.

4 DISCUSSION

The depth profile of a sample presented in **Figure 1** indicates formation of a thin carbon film. Unfortunately, the AES technique does not recognize hydrogen but since methane was used to deposit the film it is expected that it contains much hydrogen. Namely, methane molecules entering the discharge are not only partially ionized but also well-dissociated. The dissociation products are neutral H atoms and CH_x radicals. Since our plasma is not powerful, full dissociation is unlikely to

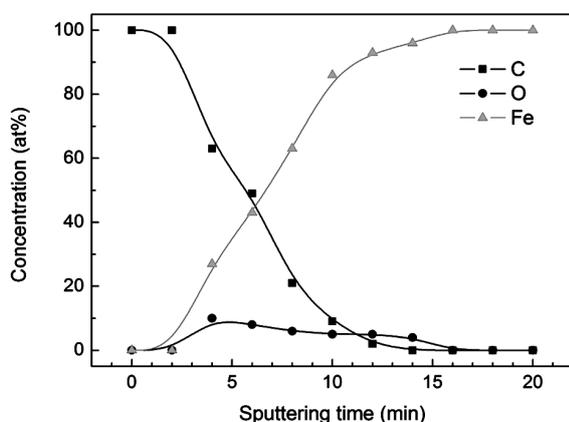


Figure 1: AES depth profile of an iron sample after exposure to methane plasma for 200 s

Slika 1: AES profilni diagram jeklenega vzorca po izpostavi metanovi plazmi za 200 s

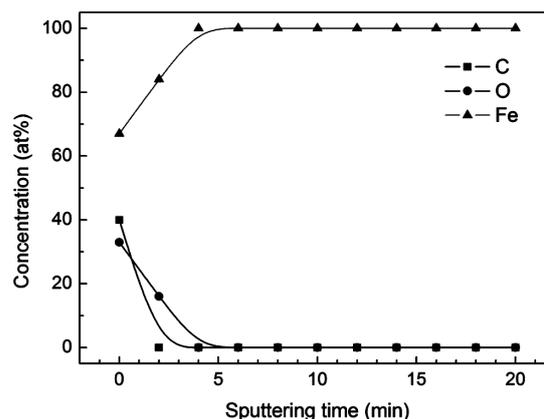


Figure 2: AES depth profile of an iron sample after exposure to methane plasma for 200s and subsequently to oxygen plasma for 12 s
Slika 2: AES profilni diagram jeklenega vzorca po izpostavi metanovi plazmi za 200 s in nato kisikovi plazmi za 12 s

occur. The CH_x radicals stick on the surfaces forming a thin film of hydrogenated carbon. The appearance of the film is easily observed with a naked eye because it is black. The thickness of the layer cannot be determined by the eye but AES depth profile gives a good approximation. The thickness is calculated from the **Figure 1** by taking into account approximate sputtering yield which was determined previously with standard samples. In our case, the thickness is estimated to about 3 nm. The deposition rate is pretty low, what can be explained either by low deposition rate or by spontaneous removal of formed layer by neutral hydrogen atoms and hydrogen ions. Namely, these particles cause slow erosion of carbon in fusion reactors⁴⁰⁻⁴⁵ and it was already shown that hydrogen plasma was suitable for removal of hydrogenated carbon prepared by other techniques⁴⁶⁻⁴⁸.

It is interesting that the oxygen concentration at the interface between iron and carbon in **Figure 1** is pretty small. According to the literature, iron tends to form a thin native oxide film spontaneously⁴⁹⁻⁵¹. The absence of

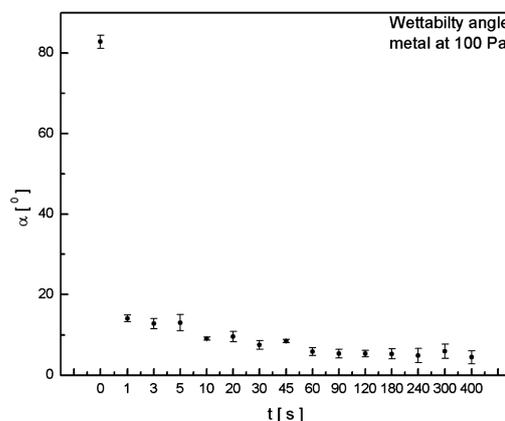


Figure 3: Contact angle of a water drop on iron samples with hydrogenated carbon deposits versus oxygen plasma treatment time.

Slika 3: Kontaktni kot vodne kapljice na jeklenih vzorcih s plastjo hydrogeniranega ogljika v odvisnosti od časa obdelave s kisikovo plazmo

rather large oxygen concentration is thus explained by effects of methane plasma. As already mentioned, lots of H atoms are created in methane plasma and these atoms cause reduction of metal oxide thin films^{52–55}. The first effect of iron exposure to methane plasma is thus reduction of the native oxide film.

Once the film is reduced the deposition of hydrogenated carbon is observed. This film is removed rather efficiently by oxygen plasma treatment as demonstrated in **Figure 2**. This sample is almost free from carbon (a small concentration is observed only at the surface and this is probably due to contamination on the way from the plasma lab to the surface characterization lab. The oxide film is now present on the surface as expected since iron is quickly oxidized after exposure to air.

Figure 3 represents results of the water drop contact angle measurements. Metals have large surface energy so the contact angle on pure metal should be very low. Samples with hydrogenated carbon deposits, however, exhibit a high contact angle, which indicates hydrophobic character of the deposits. The result is not surprising – all oxygen-free polymers are hydrophobic^{55–59}. The contact angle quickly drops at exposure to oxygen plasma as shown in **Figure 3**. The huge decrease of the contact angle after 1s of plasma treatment cannot be attributed to removal of the film, since the sample is still black. The effect is rather explained by surface functionalization of the hydrogenated carbon film. Numerous authors have shown that even a brief exposure of polymer to oxygen plasma causes an appearance of oxygen-rich functional groups on the surface of a polymer^{60–64}. These functional groups are extremely polar and the surface functionalized by them is usually hydrophilic. The contact angle shown in **Figure 3** keeps decreasing with increasing oxygen plasma treatment time and finally stabilizes at the value of approximately 10°, typical of very clean metals.

Knowing the thickness of the original hydrogenated carbon films, Δz , and length of oxygen plasma processing needed for complete removal of the film, Δt , allows for an estimation of the removal rate. The removal rate is

$$\Delta z/\Delta t = 3 \text{ nm}/12 \text{ s} = 0.25 \text{ nm/s} \quad (3)$$

This value is approximate since the removal is not all homogeneous. Also, the estimation of the film thickness is not very accurate, and finally, it is worth mentioning that this value holds for room temperature. It has been shown that removal rates of amorphous carbon deposits increase with temperature²³, so we expect that this removal rate would also be higher at elevated temperature.

5 CONCLUSION

The experimental results presented in this paper clearly show that weakly ionized oxygen plasma created in inductively coupled radiofrequency discharge is a

suitable medium for removal of hydrogenated carbon thin films. The films that were deposited by CVD using methane as precursor were effectively removed in about 10 s which makes this technique suitable for cleaning of large areas. The removal rate was estimated to about 0.25 nm/s. This value may be somewhat too small for application in fusion reactors, but it should be stressed that modern fusion devices operate at elevated temperature of few 100 °C where the removal rate is expected to be much higher.

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