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Autor: Keppner, Herbert / Kroll, Ulrich / Torres, Peter

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Process-enhancement of hydrogen-plasma treatment by argon?

by HERBERT KEPPNER, ULRICH KROLL, PETER TORRES, MICHAEL GOETZ and JOHANNES MEIER

Abstract

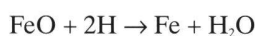
Atomic hydrogen is considered to be the key radical produced in a hydrogen plasma that leads to a chemical reduction of strongly corroded or oxidized metal objects. Hence there is a need for “soft” plasma sources that produce, on one hand, a high radical density, on the other hand, that avoid too high ion energies. The latter ones can lead to substrate damage.

The very high frequency discharge process (VHF-GD) developed at IMT (Curtins et al.¹) comes close to the ideal scope of a process that fulfils partly such a priori contradictory requirements. This process has so far been used in the fields of *plasma enhanced chemical vapour deposition* (PECVD) or plasma etching. The link between the performance of plasma chemistry and the plasma excitation frequency has been pointed out by Stan Vepřek et al.²

Using a VHF-GD parallel plate reactor, an even more pronounced production of atomic hydrogen can be observed if hydrogen is strongly argon diluted, as compared to the case when a pure hydrogen plasma is applied. However, this surprising behaviour is attributed to Argon metastable quenching of residual traces of water vapour in the rest-gas.

Introduction

The basic principle of the restoration of metal objects using plasmas is attributed to the reduction of iron oxide using atomic hydrogen, according to Vepřek et al.³ The reaction that takes place at the surface of the object is given by equation (1):



whereas the atomic hydrogen can be formed at low temperatures using a “cold” low pressure plasma; thereby electron-impact dissociation of molecular hydrogen occurs. Using conventional DC (direct current) or RF (radio frequency: 13.56 MHz, (Megahertz) driven plasma sources, the conservator of metal objects has carefully to control the plasma power in order to get a good process performance; he also has to take care to avoid overheating of the object due to too strong ion-bombardment.

It can be concluded that the use of plasmas in archaeology is a new field; it therefore makes sense to overtake

experience from technologies that already are approved for industrial purpose. Such processes are e.g. PECVD, or plasma etching. It was found^{1,4-7} that the very high frequency glow discharge technique (VHF-GD) fulfils similar requirements for PECVD, as demanded for restoration, namely a high process performance for formation of radi-

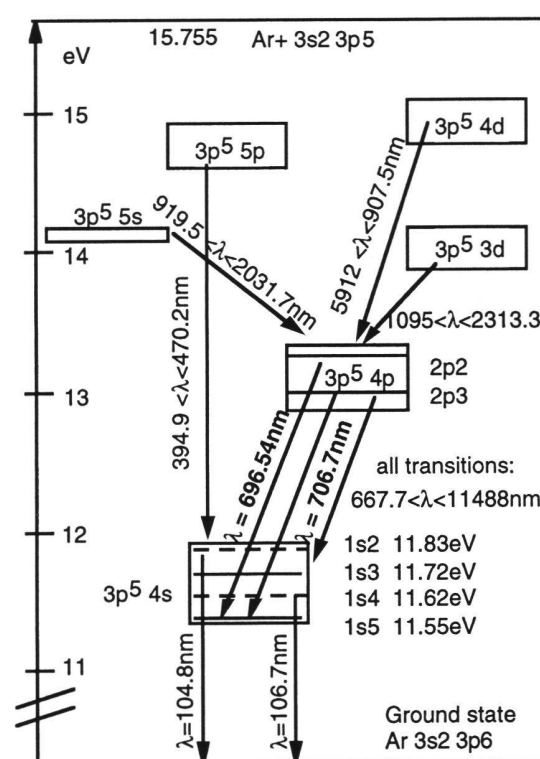
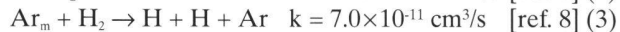
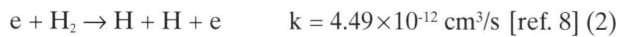


Fig. 1 Schematic representation of the energy levels of the argon atom, according to [9,10]. The transients that are marked with bold lines are related to the rate of populating of the metastable state 1s⁵.

calcs and, simultaneously, reduced substrate load due to ion bombardment. It was shown that, the more the plasma excitation frequency is increased, the more the RF power is dissipated rather to the bulk of the plasma than to the sheaths.

Hence we suggest that the VHF-GD might bring new input not only for thin-film deposition, but also for restoration.

Apart from the deposition process itself, further progress in formation of atomic hydrogen in argon / hydrogen (Ar/H_2) mixtures could come from an additional dissociation channel that is not only based on electron impact [as described by equation (2)], but on quenching of metastable argon atoms according to equation (3):



It is the objective of this paper to verify experimentally if an important enhanced atomic hydrogen production can be obtained using argon dilution. If this would be the case, a suitable mixture of hydrogen and argon could lead to a stabilization of the plasma on one hand, on the other hand to a better production rate of atomic hydrogen.

Experimental

All the experiments were carried out in a parallel plate reactor as shown in Fig. 2. This set-up is not typical for

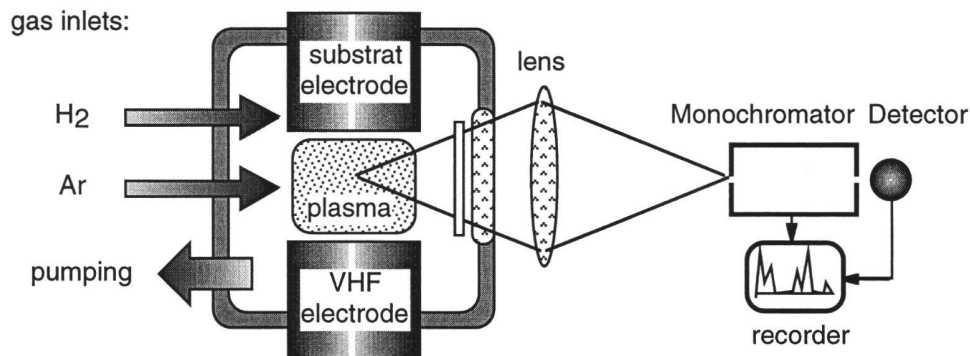
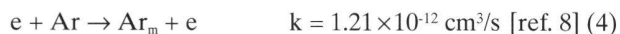
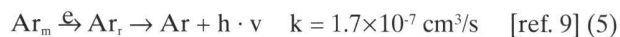


Fig. 2 Experimental set-up of the VHF-GD reactor used with gas supply, pumping system, VHF-power supply, and the set-up for optical emission spectroscopy (OES).

The formation of metastables, again, is via electron impact given by equation (4):



The schematical sketch given in Fig. 1 shows the energy levels of argon, whereby the bold lines represent examples of transitions that lead to the population rate of the metastable states ($1s^3$ and $1s^5$). The transition from a metastable state to the ground state is forbidden due to selection rules, hence its lifetime is strongly enhanced as compared to resonant states and by that the probability to undergo quenching reactions that lead to dissociation of molecular gases, increases. Apart from quenching reactions, metastable states can be converted to a resonant state due to electron impact as given in equation (5). This reaction is a loss reaction for metastable states.



From Fig. 1 it can be seen that the formation of argon metastables needs “hot electrons”. In order to obtain a notable contribution of dissociation, the gas (in our case hydrogen) should be strongly argon diluted in order to reduce losses of “hot electrons” via dissociation or excitation channels.

restoration purposes as proposed by Vepřek et al.³; it is in this special case used to bring insight to the role of metastable quenching of hydrogen.

The reactor is equipped with gas inlets (hydrogen and argon), a pumping system and VHF-(very high frequency) power supply, and the matching network. In order to detect the formation of atomic hydrogen, OES (optical emission spectroscopy) was applied; whereby the intensity of the emission line at 656 nm (nanometer) was used as “finger-print” for the formation of atomic hydrogen. For the experiments the pressure and the gas flow of hydrogen and argon was varied; furthermore the experiments were carried out at two different electrode temperatures (room temperature and 220°C).

Results and Discussion

Fig. 3 shows a typical OES from a hydrogen / argon plasma. With respect to our study, only the most important lines of the emission spectrum of the plasma of the gas mixture are mentioned:

The ensemble of lines at the left and the right side of 603 nm is the so called *Fulcher regime* with its most intense line at 603 nm. These *Fulcher lines* come from the excitation of molecular hydrogen (H_2) and are not of interest for our study. For our evaluation we are more interested for atomic

hydrogen which has a strong emission line at 656 nm. We assume that the intensity of this line is proportional to the steady-state concentration of produced atomic hydrogen. The intensities of the two argon lines at 696 and 707 nm are attributed to the population rates of the $1s^5$ metastable states of argon. There is no direct monitor for the concentration of metastable states; apart from the quenching reaction given by equation (3), these states are transformed with a high probability into resonant states according to equation (5) and lost. The emission of the H 656 nm line can be attributed to H formation either due to electron impact or metastable quenching.

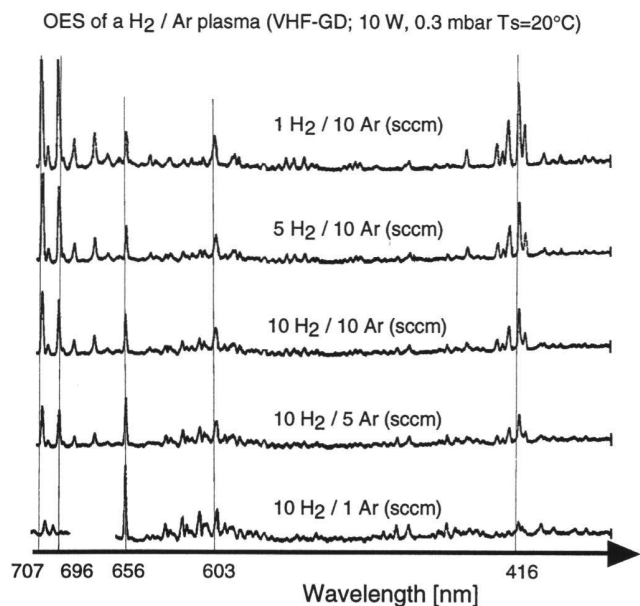


Fig. 3 Typical OES of a plasma of hydrogen/argon gas mixtures at a pressure of 0.3 mbar. As parameter, the gas-flow ratio was varied. The electrodes were kept at room temperature. (The lines at 416 nm, 707, and 696 belong to Argon, the lines at 603 and 656 nm belong to the hydrogen emission.)

All the measurements on OES are given by Figs. 4, 5. In Fig. 4, the low pressure case (0.3 mbar) and an electrode temperature at room temperature is represented. As parameter, the feed-gas flow-ratio hydrogen/argon was varied. We observe that the production of atomic hydrogen (expressed by the H 656nm line) scales estimatively with the partial pressure of molecular hydrogen. Inversely, with decreasing partial pressure of argon, all argon lines decrease as well. In Fig. 5, which represents the high pressure case at 0.9 mbar, the conditions are significantly different: the H 656 nm line has highest values at the lowest hydrogen partial pressure of hydrogen (1 sccm H₂ in 10 sccm Ar, sccm = standard cubic centimeter per minute). We observe for this case an even higher H 656 nm intensity as

it can be measured for a pure hydrogen plasma at the same pressure. This phenomenon seems to suggest that, indeed, the low concentration of hydrogen in the discharge does not lead to a competing drain for “hot” electrons. Hence, more hot electrons are available to enhance reaction (4) and to produce argon metastables. However, further detailed study shows, that this is not the case: After accurate outbaking of the reactor and its electrodes at 220°C, the spectra given in Fig. 5 are qualitatively identical as the spectra given in Fig. 4. Hence, the true explanation must be looked for in the sense that the effect of enhanced atomic hydrogen emission, as observed at cold electrodes (Fig. 5)

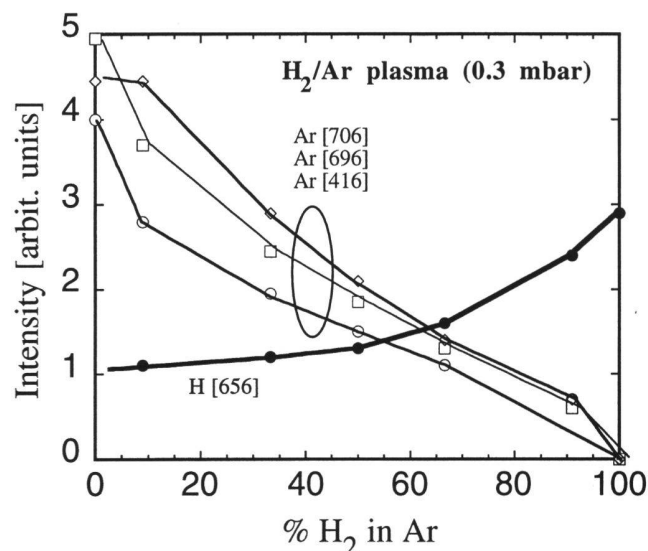


Fig. 4 Intensities of hydrogen and argon emission-lines in function of the hydrogen/argon flow at a low total pressure (0.3 mbar)

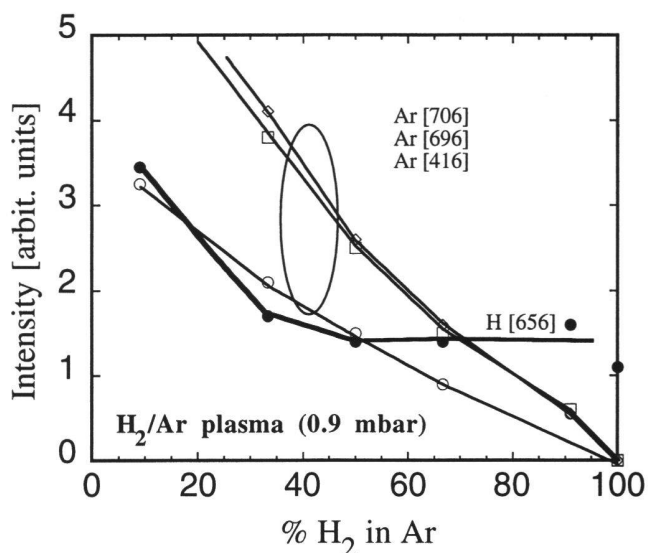
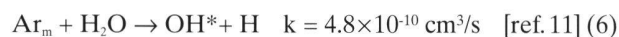


Fig. 5 Intensities of hydrogen and argon emission lines in function of the H₂/Ar flow at a higher total pressure (0.9 mbar) and cold electrodes. Note, surprisingly, in contrast to Fig. 4, the H 656 nm intensity is enhanced at low hydrogen partial pressures.

vanishes for outbaked electrodes. As well known, an outbaked reactor does no more desorb water vapour that can be considered as an additional gas source. Further studies based on the work of Ferreira et al.¹⁰ and Velazzo et al.¹¹ showed that comparing rate constants between the quenching reaction (3) and the rate constant of reaction (6) let us conclude that water vapour is a much more efficient “quencher” for argon metastables than hydrogen.

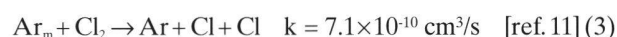


We conclude that the additional atomic hydrogen observed in the high-pressure case at room temperature electrodes comes from reaction (6).

Conclusion

In order to enhance the production of atomic hydrogen it is proposed that the Very High Frequency Glow Discharge (VHF-GD) could bring new progress for conservation of metal objects. The limit of plasma processes is due to the laws of plasma physics and chemistry that limits the dissociation process of molecular gases involved. However, adding argon to the feed gas has the potential to stabilize the plasma and to support the process in a considerable manner, as shown in the case of PECVD (Keppner et al.¹²).

It is pointed out in this work, however, that special care must be taken if argon is added to the feed gas due to the fact that very efficient quenching reactions can take place even if small traces of certain impurities are desorbed from the object itself. These impurities can be considered as additional gas source as long as the desorption takes place and the conditions may strongly vary during the process. During the plasma treatment particle bombardment heats gradually the initially cold objects that leads to enhanced desorption and hence to an uncontrolled gas source. Apart from our discussed case where desorbed water vapour from the electrodes acts as “quencher” for metastables, a further extreme example should be mentioned here: If a strongly chlorine containing artifact is concerned, the following reaction



indicates that Cl_2 is a very efficient “quencher” and that small traces of it could lead to an unwanted reaction of the treated artifacts with atomic chlorine according to equation (7). In this extreme case, instead of a surface reduction with atomic hydrogen, as indicated by equation (1), strong etching with atomic chlorine could take place. One can summarize from this work that it is questionable whether a beneficial effect from argon metastable quenching of hydrogen can bring benefit to the process performance if hydrogen is diluted in argon; on the other hand special care must be taken to avoid unwanted reactions.

REFERENCES

- ¹ H. CURTINS / N. WYRSCH / A. SHAH, in: *Electron. Lett.* 23, 1987, p. 228.
- ² STANISLAV VEPŘEK / C. BRENDL / H. SCHÄFER, in: *J. Cryst. Growth* 9, 1971, p. 266.
- ³ STANISLAV VEPŘEK / CHRISTIAN ECKMANN / JÖRG THEODOR ELMER, in: *Plasma Chemistry and Plasma Processing* 8, No. 4, 1988, p. 445.
- ⁴ A. HOWLING / J. L. DORIER / CH. HOLLENSTEIN / ULRICH KROLL / F. FINGER, in: *J. Vac. Sci. Technol. A* 10, No. 4, 1992, p. 1080.
- ⁵ ULRICH KROLL / Y. ZIEGLER / JOHANNES MEIER / HERBERT KEPPNER / A. SHAH, *Proceedings of the MRS Symp.*, San Francisco CA Vol. 336, April 1994, p. 115–120.
- ⁶ C. BENEKING, in: *J. Appl. Phys.* 68, 1990, p. 4461.
- ⁷ HERBERT KEPPNER / ULRICH KROLL / JOHANNES MEIER / A. SHAH, in: *Solid State Phenomena Vols. 44–46*, 1995, p. 97–126.
- ⁸ M. KUSHNER, in: *J. Appl. Phys.* 63, No. 8, 1988, p. 2532–2551.
- ⁹ L. SANSONNENS / A. A. HOWLING / CH. HOLLENSTEIN / J.-L. DORIER / ULRICH KROLL, in: *J. Phys. D: Appl. Phys.* 27, 1994, p. 1406–1411.
- ¹⁰ C. M. FERREIRA / J. LOUREIRO, in: *J. Appl. Phys.* 57, No. 1, 1985, p. 82.
- ¹¹ VELAZZO / KOLTS / SETSER, in: *J. Chem. Phys.* 10, 1978, p. 4357.
- ¹² HERBERT KEPPNER / PETER TORRES / JOHANNES MEIER / R. PLATZ / D. FISCHER / ULRICH KROLL / S. DUBAIL / J. A. ANNA SELVAN / N. PELLATON VAUCHER / Y. ZIEGLER / R. TSCHARNER / CH. HOF / N. BECK / M. GOETZ / P. PERNET / M. GOERLITZER / N. WYRSCH / J. VEUILLE / J. CUPERUS / A. SHAH / J. POHL, to be published in the *Proceedings of the MRS Symp.*, Boston MA, 1996.