

Surface modification by subsurface pressure induced diffusion

Claus G. Zimmermann

Citation: [Applied Physics Letters](#) **100**, 041908 (2012); doi: 10.1063/1.3679616

View online: <http://dx.doi.org/10.1063/1.3679616>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/100/4?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Surface area and porosity in obliquely grown photocatalytic titanium dioxide for air purification](#)

J. Appl. Phys. **115**, 174907 (2014); 10.1063/1.4874918

[Electronic transport in heavily doped Ag/n-Si composite films](#)

AIP Advances **3**, 102111 (2013); 10.1063/1.4824854

[Controlled synthesis of SnO₂ nanostructures with different morphologies and the influence on photocatalysis properties](#)

J. Appl. Phys. **114**, 114302 (2013); 10.1063/1.4821140

[Case studies in surface photochemistry on metal nanoparticles](#)

J. Vac. Sci. Technol. A **31**, 050817 (2013); 10.1116/1.4818425

[Synthesis of zinc oxide powder as function of precursor concentration and their photo catalytic activity test](#)

AIP Conf. Proc. **1476**, 339 (2012); 10.1063/1.4751624

The image shows the cover of the journal 'Applied Physics Reviews'. It features a diagram of a layered structure with labels for 'p-type', 'n-type', and 'intrinsic' regions, and a graph showing 'Carrier concentration' and 'Electrical conductivity' as a function of position. The AIP logo is in the top left corner.

NEW Special Topic Sections

NOW ONLINE
Lithium Niobate Properties and Applications:
Reviews of Emerging Trends

AIP Applied Physics
Reviews

Surface modification by subsurface pressure induced diffusion

Claus G. Zimmermann^{a)}

EADS Astrium, 81663 Munich, Germany

(Received 5 October 2011; accepted 9 January 2012; published online 26 January 2012)

Polycrystalline Ag, covered with a nm thin siloxane layer, was irradiated with ultraviolet light in vacuum at 500 K. Ag particles of different aspect ratios, 50–1000 nm in size, formed on the surface, including a small fraction of nanorods. Pressurized water vapor bubbles are created in the subsurface region by hydrogen radicals photo-chemically released by the siloxane layer. They provide the driving force for a diffusive material flux along grain boundaries to the surface. This mechanism was modeled and found to agree with the experimental timescale: approximately 300 h are required for a 1000 nm particle to form. © 2012 American Institute of Physics.
[doi:10.1063/1.3679616]

There are several ways to create non-equilibrium surface structures on a sub-micron scale, ranging from the deposition of nanoparticles produced in the gas phase,¹ to ion beam bombardment² and sputtering.³ But also processes occurring in the bulk can alter the surface morphology. On the one hand, pressurized voids are formed after hydrogen exposure of steels⁴ or ion implantation of metals⁵ and semiconductors.⁶ The pressure in these voids is estimated to be in the range 10^8 – 10^9 Pa,^{4,6,7} which results in plastic deformation of the surrounding material and blister formation on the surface. The internal nitridation of nickel alloys⁸ or the internal oxidation of Ag-In alloys⁹ at temperatures above 800 K on the other hand are examples where several μm large surface protrusions are formed by an outward dislocation pipe diffusion of matrix atoms, driven by the volume increase of the nitride or oxide formation. These processes by themselves are ill-suited for a controlled surface modification, since either the pressure or the temperature is too high.

The approach of this work is to combine them at lower temperatures to facilitate a deliberate surface modification by a diffusion controlled material transport to the surface, which originates from pressurized voids introduced photo-chemically in the subsurface region. Polycrystalline Ag has been chosen as a model system, since pressurized water vapor bubbles can be formed easily. By exposing polycrystalline Ag subsequently to oxygen and hydrogen atmospheres for 1–2 h at 1070 K, water vapor bubbles are formed throughout the bulk of the material and are located preferentially at grain boundaries.^{10,11} On the surface, voids are observed, thought to be the result of violent eruptions of the water vapor through the surface.^{12,13} For polycrystalline Ag catalysts, these surface reactions have been studied in detail. The violent void formation was observed to start ≈ 700 K, in hydrogen,¹⁴ water vapor,¹³ and methanol/oxygen¹⁵ vapor at pressures $\approx 5 \times 10^2$ Pa.

In order to achieve the desired significantly lower temperatures and void pressure levels, combined with an independent control of Ag diffusivity and hydrogen flux in the material, the hydrogen radicals in this work were produced photochemically rather than thermally. 50 μm thick, 5 mm wide stripes of 99.9% pure, polycrystalline silver foils,

supplied by HERAEUS, were bonded with a 80 μm thick layer of the methyl-phenyl siloxane, NUSIL CV10-2568 to an Al plate covered by a Kapton foil. In addition, $\approx 1 \text{ cm}^3$ cured siloxane spots were placed next to each Ag stripe. This assembly, positioned on a temperature controlled base plate, was irradiated in a 10^{-6} Torr vacuum by ultra-violet (UV) light with an average power density of 1200 W/m^2 in the 200–400 nm wavelength region for 1000 h. Further details on the setup and lamp spectrum can be found in Ref. 16. The Ag foil reached a temperature of 500 K during illumination.

By outgassing of short chain length fragments, a siloxane layer is deposited on surfaces during UV exposure. A 4 nm thick film was detected after test by Fourier transformed infrared spectroscopy (FTIR) on a CaF_2 window at 500 K in the vicinity of the samples. On the Ag foil itself, a x-ray photoelectron spectroscopy (XPS) sputter depth profile revealed a ≈ 5 nm siloxane layer on the surface. In addition, an average of 10 at. % oxygen was detected over the measured depth of 30 nm. The siloxanes show a pronounced absorption peak around 260 nm due to the presence of the phenyl groups.¹⁶ Taking their detailed absorption characteristic and the UV lamp spectrum into account, they absorb 61 W/m^2 . This is equivalent to a flux Φ of $8.9 \times 10^{19} \text{ m}^{-2} \text{ s}^{-1}$ 260 nm photons. Their energy is well above the energy required for C-H bond cleavage. A quantum yield η of 0.63×10^{-5} H radicals per incident photon was measured.¹⁷ In nm thin films, the lifetime of the H radicals is sufficient to escape the film¹⁸ before abstracting another H atom.

The Ag surface exhibits a highly non-equilibrium surface structure after exposure as illustrated in the scanning electron microscope (SEM) image in Fig. 1(a). Particles with different aspect ratios have formed in a wide size range from 50–1000 nm. A small fraction of nano-rods is observed, several μm long and 50–100 nm in diameter. In contrast, non-illuminated areas, for example, small regions on the rear side of the foil that were not bonded to the support plate, remained completely unaffected. The particles are preferentially aligned along surface defects, in particular along the rolling structure of the foil, as shown in Fig. 1(b). The particles could be easily removed by an adhesive tape. This revealed pits in the Ag surface, up to 1 μm in size. Through the pits, individual Ag grains are visible, as illustrated in Fig. 1(c). Energy dispersive x-ray (EDX) analysis performed

^{a)}Electronic mail: claus.zimmermann@astrium.eads.net.

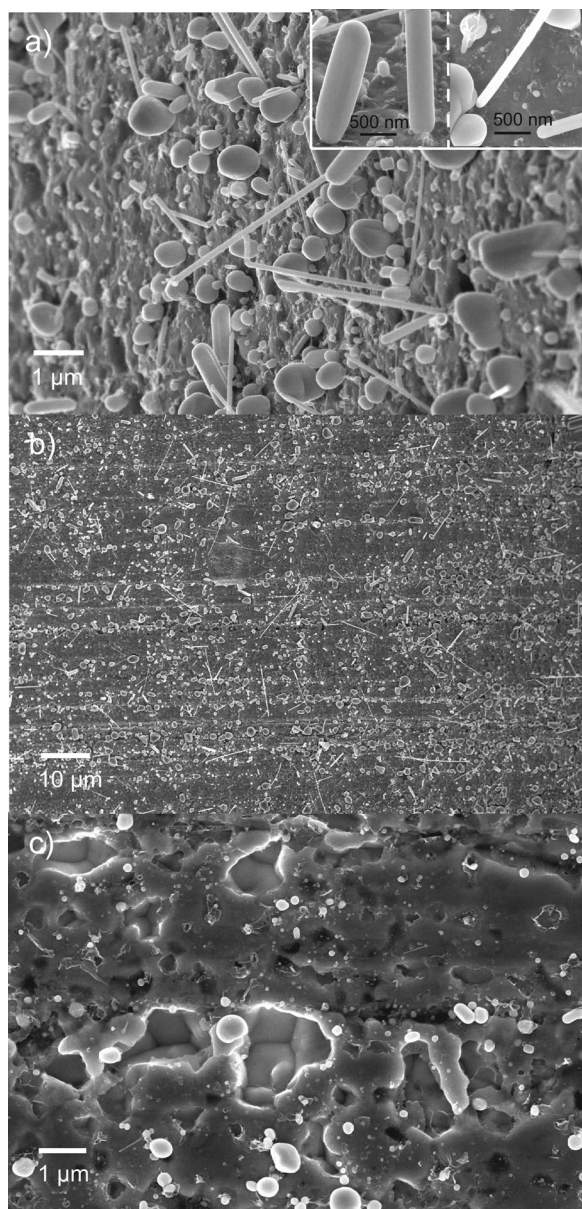


FIG. 1. SEM images of (a) the Ag surface after 1000h UV exposure at 500 K, (b) low magnification overview, and (c) Ag surface after the particles were removed by an adhesive tape. Note that the images are not from exactly the same area. The inset shows some particles in higher magnification.

on the particles removed confirmed that they are composed of pure Ag. A scanning transmission electron microscope (STEM) image of the Ag foil in cross section, prepared by a focused ion beam, is illustrated in Fig. 2. The Z contrast image in combination with STEM EDX corroborates the

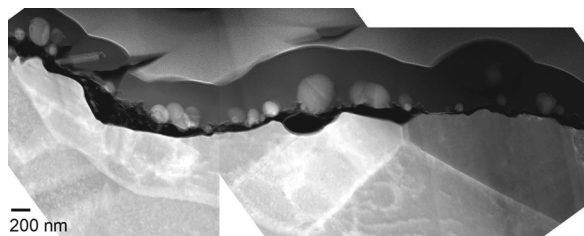


FIG. 2. Z contrast STEM image of a cross section through the particle covered Ag film.

SEM results. The Ag particles are loosely attached to the Ag foil, in the vicinity of pits.

The rounded, cap like shape of even the high aspect ratio particles, shown magnified in Fig. 1(a), as well as the Ag ceiling still present at the edge of the pits in Fig. 1(c), are not in line with a push out of grains by grain boundary sliding similar to a mechanism believed to be active during whisker growth.¹⁹ The particles rather must have formed through a diffusive material flux. Their shapes resemble those observed in the chemical synthesis of Ag nanoparticles, e.g., by the polyol process.²⁰ In particular, the growth of nanowires in these methods was attributed to the action of a surfactant.²¹ Speculatively, the silicone coating, visible in the SEM images of the Fig. 1(a) inset, and confirmed by the XPS surface measurements, might have played a similar role here. A detailed explanation, however, is beyond the scope of this work.

To model the material transport to the surface, an idealized cylindrical grain with radius d and height d is considered with a spherical void of radius r at the center of the cylinder base. Hydrogen radicals created on the surface and oxygen present in the near surface region diffuse very rapidly. The diffusivity of hydrogen²² as well as of oxygen²³ in Ag at 500 K is in the $10^{-10} \text{ m}^2 \text{ s}^{-1}$ and $10^{-11} \text{ m}^2 \text{ s}^{-1}$ range, respectively, and exceeds the Ag self diffusivity by more than 10 orders of magnitude.²⁴ Solely in the void, they react to form water. Like for methane formation in steel,⁴ only the void provides ample space to accommodate the larger H_2O molecules, which get trapped. This chemical reaction lowers the H and O concentration around the void and drives the diffusion of additional radicals there. Together with the very low solubility of H in Ag at 500 K,²⁵ the assumption can be made that as soon as a hydrogen radical is created on the surface, it contributes to the formation of a H_2O molecule in the void.

For simplicity, a circular area on the surface of radius $2d$ is assumed to interact with the void. Therefore, over the course of the time t , $2\pi d^2 \Phi \eta t$ H_2O molecules are added to the void. If the water molecules are treated as ideal gas, the pressure p inside the void is

$$p = \frac{3d^2 \Phi \eta k T}{2r^3} t - \frac{2\gamma}{r}, \quad (1)$$

where T denotes the temperature and k the Boltzmann constant. The second term in Eq. (1) is the opposing pressure exerted by the newly created Ag surface with a surface energy γ . The pressure p increases the chemical potential μ of Ag atoms with a volume V_m inside the void by $V_m p$, and drives the diffusion of Ag atoms to the surface. Void nucleation is not considered here. It is assumed that at a time t_0 and a corresponding size r_0 , p is positive. Due to the cubic r —dependence of the first term in Eq. (1), such conditions will always be reached, in line with the experimental observations that water vapor bubbles are nucleated easily.^{10,11}

At 500 K, the grain boundary diffusivity δD_{gb} of Ag is $2.2 \times 10^{-24} \text{ m}^3 \text{ s}^{-1}$, 300 times as large as the bulk diffusivity.²⁴ For void sizes up to $d = 500 \text{ nm}$ considered here, grain boundary diffusion thus dominates, although bulk diffusion will eventually contribute to the final stage of void growth.

By making use of the conservation of mass, the outward current of Ag atoms along the grain boundary can be calculated. It governs the change in void radius with time t . The resulting differential equation can be transformed with the help of r_0 and t_0 in a dimensionless form and solved numerically. In good approximation, an analytical solution is given by

$$t = \begin{cases} \frac{4\gamma}{3d^2\Phi\eta kT} r^2 & \forall r \leq r_c \\ \frac{2}{3d\sqrt{\Phi\eta V_m\delta D_{gb}}} r^3 & \forall r > r_c \end{cases}; r_c = \frac{2\gamma}{kTd} \sqrt{\frac{V_m\delta D_{gb}}{\Phi\eta}}. \quad (2)$$

In combination with Eq. (1), the pressure p inside the void is obtained

$$p = \begin{cases} 0 & \forall r \leq r_c \\ dkT \sqrt{\frac{\Phi\eta}{V_m\delta D_{gb}}} - \frac{2\gamma}{r} & \forall r > r_c. \end{cases} \quad (3)$$

For $r \ll r_c$, material transport is no issue. The net pressure inside the void remains zero and the void growth is governed by the surface energy term. In contrast, for $r \gg r_c$, void growth is dominated by the material transport. The cross over radius r_c depends on the ratio of water vapor production rate $\Phi\eta$ and grain boundary transport capability $V_m\delta D_{gb}$.

With a Ag surface energy²⁶ of 1.2 J/m² and a grain size d of 500 nm, r_c is 175 nm. According to Eq. (2), it takes 332 h for the void to grow to the surface and the maximum pressure during the latter phase is 9 MPa. This agrees very well with the timescale of the experiment and the pressure stays well below the yield strength of the material. $\approx 7 \times 10^{20}$ /m² H and O atoms are required in total, which is in agreement with the measured availability. The violent surface explosions observed on Ag catalysts¹³ at 700 K are also in line with this model. Equation (3) predicts a void pressure in the GPa range in this case.²⁷

In summary, internal compressive stress can be generated by photochemical hydrogen production in a regime not accessible by alternative bulk process like internal precipitation, ion implantation, or hydrogen production via a thermal route. The water vapor bubbles created in the near surface region have been shown to serve as a well controllable source of bulk material to create non equilibrium surface structures. The proposed process can likely be applied to a

range of material systems with different grain structures and be adjusted in a very wide, independent parameter space. The grain boundary diffusivity is strongly temperature dependent, the photon flux Φ can be varied over several orders of magnitude, especially with the help of lasers, and the quantum efficiency η can also be increased significantly by using shorter wavelength UV light or other ionizing radiation. Finally, a surface patterning by only illuminating certain areas is easily achievable.

¹C. G. Zimmermann, K. Nordlund, M. Yeadon, J. M. Gibson, R. S. Averback, U. Herr, and K. Samwer, *Phys. Rev. B* **64**, 085419 (2001).

²S. A. Norris, J. Samela, L. Bukonte, M. Backman, F. Djurabekova, K. Nordlund, C. S. Madi, M. P. Brenner, and M. J. Aziz, *Nature Commun.* **2**, 276 (2011).

³W. L. Chan and E. Chason, *J. Appl. Phys.* **101**, 121301 (2007).

⁴S. M. Schlögl, J. Svoboda, and E. Van der Giessen, *Acta mater.* **49**, 2227 (2001).

⁵M. Kaminsky and S. K. Das, *J. Appl. Phys.* **49**, 5673 (1978).

⁶L.-J. Huang, Q.-Y. Tong, Y.-L. Chao, T.-H. Lee, T. Martini, and U. Gösele, *Appl. Phys. Lett.* **74**, 982 (1999).

⁷B. Terreault, G. Ross, R. G. St.-Jacques, and G. Veilleux, *J. Appl. Phys.* **51**, 1491 (1980).

⁸S. Y. Chang, U. Krupp, and H.-J. Christ, *Mater. Sci. Eng., A* **301**, 196 (2001).

⁹S. Guruswamy, S. M. Park, J. P. Hirth, and R. A. Rapp, *Oxid. Met.* **26**, 77 (1986).

¹⁰S. H. Goods and W. D. Nix, *Acta Metall.* **24**, 1041 (1976).

¹¹R. L. Klueh and W. W. Mullins, *Trans. Metall. Soc. AIME* **242**, 237 (1968).

¹²X. Bao, G. Lehmppfuhl, G. Weinberg, R. Schlögl, and G. Ertl, *J. Chem. Soc., Faraday Trans.* **88**, 865 (1992).

¹³G. J. Millar, M. L. Nelson, and P. J. R. Uwins, *J. Chem. Soc., Faraday Trans.* **94**, 2015 (1998).

¹⁴L. Lefferts, J. G. van Ommen, and J. R. H. Ross, *Appl. Catal.* **34**, 329 (1987).

¹⁵G. J. Millar, M. L. Nelson, and P. J. R. Uwins, *J. Catal.* **169**, 143 (1997).

¹⁶C. G. Zimmermann, *J. Appl. Phys.* **103**, 083547 (2008).

¹⁷S. Siegel, R. J. Champetier, and A. R. Calloway, *J. Polym. Sci.* **4**, 2107 (1966).

¹⁸S. Siegel and T. Stewart, *J. Phys. Chem.* **73**, 823 (1969).

¹⁹J. Smetana, *IEEE Trans. Electron. Packag. Manuf.* **30**, 11 (2007).

²⁰B. Wiley, Y. Sun, and Y. Xia, *Acc. Chem. Res.* **40**, 1067 (2007).

²¹X. Sun and Y. Li, *Adv. Mater.* **17**, 2626 (2005).

²²W. Eichenauer, H. Künzig, and A. Pebler, *Z. Metallkd.* **49**, 220 (1958).

²³V. M. Gryaznov, S. G. Gul'yanova, and S. Kanizius, *Russ. J. Phys. Chem.* **47**, 1517 (1973).

²⁴R. E. Hoffman and D. Turnbull, *J. Appl. Phys.* **22**, 634 (1951).

²⁵E. W. R. Steacie and F. M. G. Johnson, *Proc. R. Soc. London, Ser. A* **117**, 662 (1928).

²⁶L. Vitos, A. V. Ruban, H. L. Skriver, and J. Kollár, *Surf. Sci.* **411**, 186 (1998).

²⁷A hydrogen vapor pressures of 5×10^2 Pa translates into a flux Φ of 2.5×10^{25} molecules m⁻² s⁻¹. Even with a sticking and conversion coefficient η as low as 10^{-4} , a void pressure of 3.2 GPa results.