Nanostructuring of surfaces using anodic alumina masks – methods, materials and properties

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ABSTRACT

Nanostructured surfaces gain more and more interest due to their significant change in properties caused by those nanoscale features in the surface. Processes to nanostructure surfaces are very often highly sophisticated. By using nanoporous alumina one can easily structure surfaces in the range of 20 nm to 400 nm. The features created are little pillars in the size of the pore separated by again a pore diameter spacing. Since there is no order the stochastic nanostructures exhibit very distinct properties with respect to wettability and reflectivity. When using low energetic surfaces like PTFE the wetting can drastically be changed by changing the feature size of the surface structure. Thus contact angles against water of more than 150° can be achieved. On the other hand a drop of water moves almost freely on those surfaces given rise for easy-to-clean properties. When structuring transparent polymeric samples, the legit reflection is decreased by 5 to 8 % which is new a method to produce anti-reflective shielding for automotive or even solar energy applications.

Keywords: Nanostructured surfaces, anti-reflective surfaces nanoporous alumina, injection molding.

1 NANOPOROUS ALUMINA

Since many decades the process of anodizing aluminum has been used to increase wear and corrosions resistance of the metal. The fact that distinct pores are formed during potentiostatic oxidation has been rather an obstacle to those properties. The mechanism of pore formation and pore size control has been reviewed intensively and will not be mentioned here [1,2]. In the past decade the porous structure of anodic alumina has become important with respect to applications in nanoscience and nanotechnology. Since the pore diameter can easily be controlled by varying the anodic potential (1 V anodic potential is equal to app. 1.5 nm pore diameter) [2] there is a way to simply create nanostructured composites with features between less than 10 nm and more than 400 nm. In Figure 1 a scanning electron microscopy image of a porous alumina surface is given. The samples made with 40 V anodic potential consists of pores in the order of 60 nm in diameter separated by again app. 60 nm each.

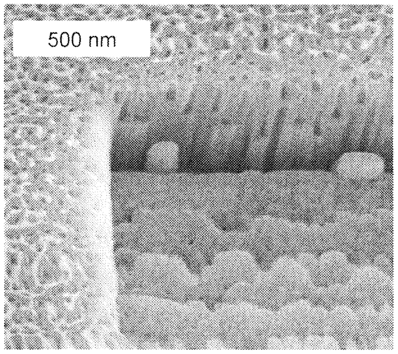

Figure 1: SEM image of a 60 nm pore size alumina surface made by anodic oxidation – perspective view of an ion etched sample

Those pores run more or less parallel throughout the layer as can be seen in Figure 2:

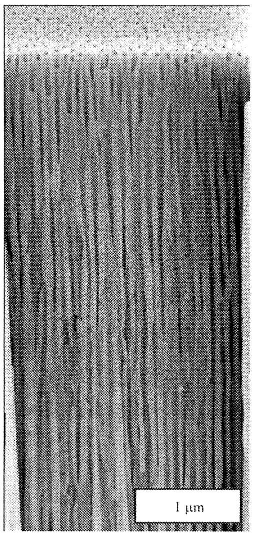

Figure 2: SEM image of a 120 nm pore size alumina surface made by anodic oxidation – cross section

When thinking about this material with respect to nanotechnology intensive work has been done in filling the pores with various materials thus creating one-dimensional magnetic or electrical or semi-conduction wires separated and well controlled in diameter and length. Also using this technology to locally deliver drugs by varying pore size and diffusion rate is another example for nanotechnological approaches. A new and very promising field to apply this technology is to use nanoporous alumina as a mask for injection molding or imprinting given rise for the easy and reproducible formation of nanostructured polymeric surfaces.

2 MOULDS, STAMPS, AND REPLICAS

Since the pore diameter can be adjusted as desired by varying the anodic potential porous alumina masks with pore diameter in the order of half a wave length of optical light or less can be made routinely. When using polished samples mirror like surfaces with a stochastic nanoporous surface can be made like the one seen in Figure 3:

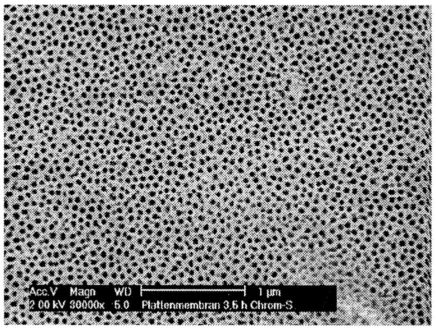

Figure 3: SEM Top view of a polished and oxidized alumina mask

Those stamps or forms are used to structure thermoplastics like PMMA, PP, PTFE and others.

2.1 PMMA

When using this alumina stamp as a master for example PMMA can be nanostructured very easily. For this the PMMA is heated above the glass transition point and the stamp is pressed against the PMMA plate after a certain contact time the pressure is released and the process is completed. In figure 4 a atomic force microscopy image of nanostructured PMMA surface is given using a 50 nm pore sized plate.

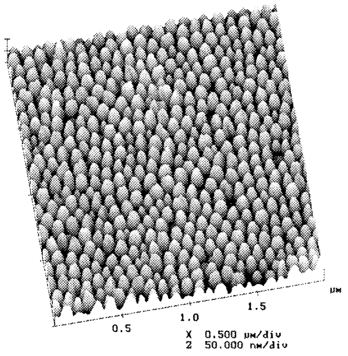

Figure 4: AFM Image of a nanostructured PMMA surface – pillar diameter 50 nm

As can be seen the surfaces is structured very regular with a dense layer of small pillar exhibiting an aspect ratio of app. 1. When using a larger pore diameter as a mask the pillars are created the same way now showing a diameter of 200 nm and again an aspect ration of app. 1. (Figure 5)

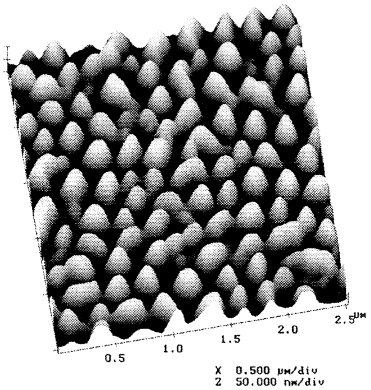

Figure 5: AFM Image of a nanostructured PMMA surface – pillar diameter 200 nm

On this sample the optical transparency has been measured. In figure 6 a comparison of the structured and unstructured sample is given.

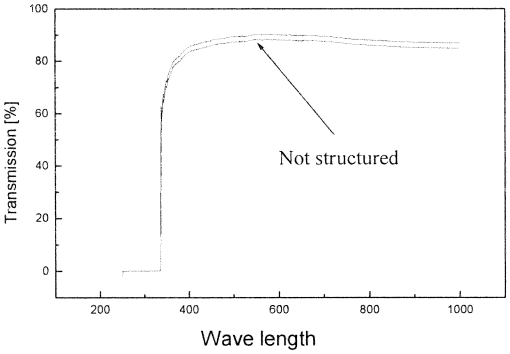

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Figure 6: Transmission spectra of a unstructured and a structured PMMA sample – incidence angle 90°

The transparency is increased by app. 2- 3% over the whole spectral range by just structuring one side. This effect can be doubled when structuring both sides of the plate. It is the well known moth eye effect which is caused by the nanometer sized pillars. Those pillars cause the refractive index of the border zone to change continuously so that the light is rather transmitted through then reflected.

2.2 PTFE

The wettability is strongly influenced by surface chemistry and surface structure. Theories derived from textiles developed by Wetzel describe the wettability of rough surfaces by introducing a correction factor into Young's equation [3]:

$$\cos\theta_{rough} = F \cdot \cos\theta_{smooth} \tag{1}$$

Later on fractal structures have been associated with the change in wettability and again Young's equation has been modified by introducing a term indication the fractal character of the surface structure [4, 5].

$$\cos\theta_{fractal} = \left(\frac{L}{l}\right)^{D-2} \cdot \cos\theta_{smooth} \tag{2}$$

L and l indicate the upper and lower limit of the fractal structure sizes while D is the fractal dimension.

Up to now no consistent theory does exits to describe quantitatively the relation between surface structure, surface energy and wettability. With the discovery of the so called "lotus leave phenomena" surface structure and wettability again became an interest of industrial and scientific research. The lotus leave exhibits structures in the range of 10 – 60 µm and on top small wax crystals of 150 nm to 300 nm in size causing the water repellent super hydrophobic properties [6, 7]. When miming such a surface methods must be at hand to structure surfaces in the range of the wax crystal size. When using nanoporous alumina surface features with sizes well below 300 nm can be made and their influence on the wettability can be examined. In Figure 7 an image of a PTFE surface with pillars in the range of 150 nm is given.

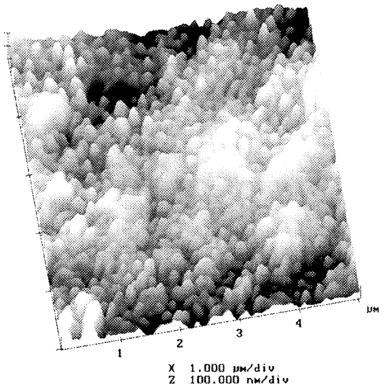

Figure 7: AFM Image of a nanostructured PTFE surface – pillar diameter of app. 150 nm

When varying the pillar size the contact angle against after can be increased from 110° for PTFE itself up to more than 140° for a structured sample. As the feature size increases the contact angle increases as well as can be seen in Figure 8.

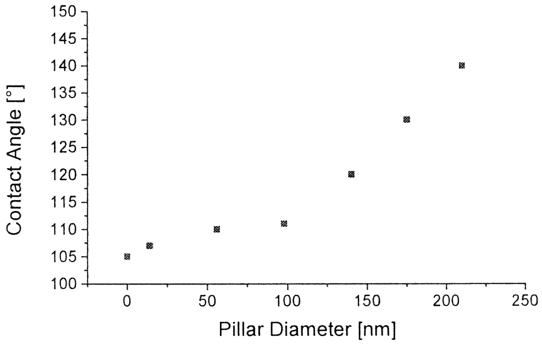

Figure 8: Contact angle against water as a function of pillar diameter

Below 100 nm the wettability is only slightly increases. Here the feature size seems to be to small to significantly influence the water drop in the surface. When further increasing the diameter the contact angle increases finally up to mire than 140° for pillars of 225 nm in diameter.

3 SUMMARY

When using nanoporous alumina polymeric material can routinely be nanostructured either by stamping or injection molding. The feature size of the surface structure can be varied between 20 nm and more than 400 nm. By this surface and materials properties can be modified. When structuring low energetic surfaces like PTFE the wettability is decreased. When using high energetic surfaces it can be increased the same way.

Optical transparent materials like PMMA or PC or others can be structured to reduce the light reflection caused by the change in refractive index at the borderline of the material surface.

Beside soft materials, metals like Platinum, Palladium or others can also be structured which might open new ways in heterogeneous catalysis.

REFERENCES

[1] R. C. Furneaux, W. R. Rigby, A. P. Davidson. Nature 1989, 337, 147-149.

[2] J.P. O`Sullivan, , Proceedings of the Royal Society of London, 317, 511 - 549, 1970

[3] A.B.D. Cassie, S.Baxter, Wettability of Porous Surfaces, Transactions Faraday Society, 40, 546-551,1944

[4] R.D. Hazlett Fractal Applications: Wettability and Contact Angle, Transactions Faraday Society, Journal of Colloid and Interface Science, 137, 527-533, 1990

[5] T. Onda, S. Shibuichi, N. Satoh, K. Tsujii, American Chemical Society Langmuir, 12, (9), 1996

[6] W. Barthlott, , Klima- und Umweltforschung an der UNI Bonn, 116-120, 1992

[7] W. Barthlott, C. Neinhuis, , Planta, 202, 1-8, 1997