Concentration of Information

Nano-replication. In the optimisation of optical storage media, miniaturisation will continue to be a key aspect of development. A recent research project examined the influence of different masters and moulding compounds on the replication accuracy of nanostructures.

Increasing the storage density of optical media such as CDs is not possible without additional miniaturisation of the surface structures – the so-called ‘pits’. In the search for new injection moulding compounds and for evaluating new masters, precise replication of these pits on the nanometer scale has thus, to a certain extent, become a prerequisite.

As part of a research project for Bayer MaterialScience AG, Leverkusen/Germany, different moulding compounds and various kinds of masters (wafers and stampers) were examined for their potential to replicate nanostructures. Plastic discs with a diameter of 80 mm and a thickness of 1.2 mm, which had been used in earlier tests, were chosen as the mouldings [1, 2, 3]. The surfaces of these plastic discs contain different structures that can vary according to the master that has been used. A master is a disc-shaped mould insert for the injection mould that has been provided with surface structures. The surface structures of the masters consist predominantly of V-shaped pits or grooves. The structures are in both the micro/submicro range and in the nanometer range. In addition to these V-shaped pits, U-shaped pits and Λ-peaks are also employed as master structures for replication in plastic. Frequently used masters include Si wafers with micro V grooves, Ni stampers with micro V grooves (Ni stamper directly processed from Si wafer), Ni stampers with CD-R groove (corresponds to the CD-R stamper) and Ni stampers with nano-V grooves (Ni stamper directly processed from Si wafer and second Ni galvanisation from Ni stamper).

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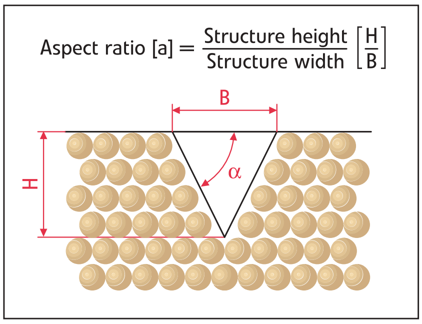

Fig. 1. Formation of V-pits starting from a surface with a crystal structure of <100>

Production and Structuring of the Masters

An Si wafer is produced by anisotropic wet etching. This involves taking a silicon monocrystal and etching V-shaped pits with a defined geometry and very sharp – ideally, atomically sharp – tips into it. With the aid of specific etching solutions, the material is removed at different speeds, depending on the crystal orientation. The ratio of the etching removal perpendicular to the surfaces <100> and <111> is approx. 400:1. In the case of a silicon monocrystal with an orientation of <100> on the surface, individual atomic layers are, according to this principle, continuously removed. This results in V-shaped pits on the Si surface whose aspect ratio is governed by this lattice structure. The aspect ratio a describes the ratio between the height H and the breadth B of the structure (Fig. 1). In the case of the wafer used here with the <100> lattice structure on its surface, this results in an aspect ratio of 0.707 [4].

The exposing mask for the structuring is produced in a mask shop from the mask design. The structure design corresponds to the arrangement of the different structural areas (Fig. 2). To prepare the wafer, the silicon is oxidised (SiO_2 layer, thickness 120 ± 1 nm) and subsequently machined. Before exposure, the wafer is given a resistant coating, also known as lacquering. Alternatively, a photo resist can be used as a positive resist for optical lithography (thickness: approx. 400 nm) or PMMA for electron beam lithography (thickness: approx. 60 nm).

In the next step, the so-called etched windows are generated in this layer (Fig. 3). For this purpose, the wafer is exposed using a mask aligner. The exposed resists are dissolved out during subsequent development.

For transferring the structure, the structure of the etched window is transferred to the oxide layer by reactive ion etching (Fig. 4). The final structures are

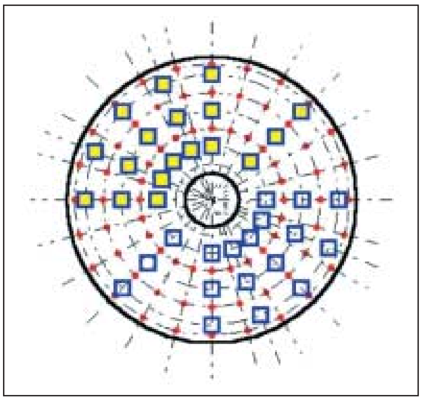

Fig. 2. Arrangement of the structures

etched into the silicon by wet etching with potassium hydroxide. Finally, the SiO_2 layer is removed with hydrofluoric acid. For use in an injection mould, an anti-adhesive coating must also be applied to prevent the plastic sticking to the wafer.

From Si Wafer to Ni Stamper

An initial layer of gold is applied to a structured Si wafer. After this comes the Ni galvanisation, i.e. from a silicon wafer with V-pits we get a nickel disc with Λ-peaks. If this is placed directly into a moulding tool, we get V-pits in the polymer. These negative structures are difficultly accessible for profile measurement. Only through subsequent galvanic replication of the first galvanisation process is a nickel disc produced that has the same structural profile as the original (Fig. 5). During replication, this results in Λ-peaks, which can be easily measured because of their positive form. Ni galvanisation has a high replication fidelity. Dimensional deviations are virtually impossible to detect even by AFM measurements (Fig. 6).

For structures up to approx. 2 µm wide, photolithography with commercial mask aligners can be used. Their advantage is that, with industrial E-beam lithography machines or optical pattern generators, a mask only has to be produced once and can then be used for exposures several

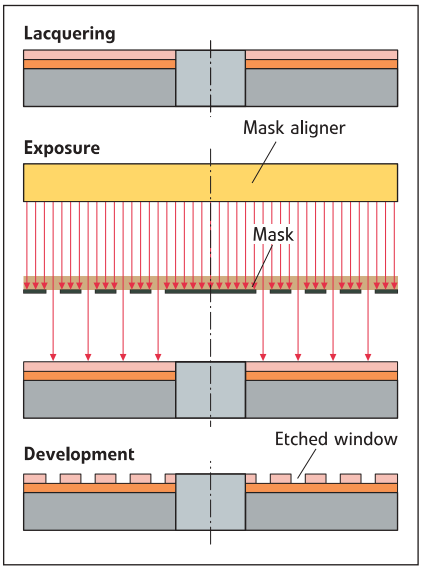

Fig. 3. Lithography

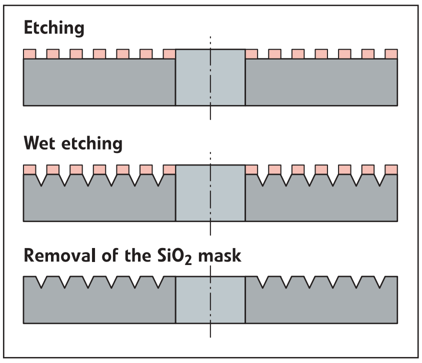

Fig. 4. Structure transfer

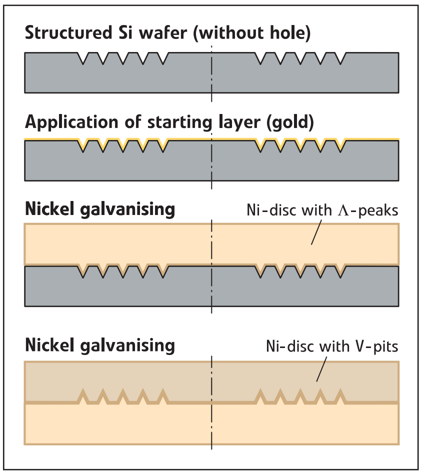

Fig. 5. Production of the Ni stamper with micro V-pits from a Si wafer

times. The absorption pattern of the mask is exposed in parallel into the resist within a few seconds on a scale of 1:1.

For narrower structures down to a range of less than 100 nm, use can generally only be made of special optical exposure processes, which utilise the interference effects of coherent laser beams or serial recording processes with particles or electrons as probes, e.g. E-beam lithography. The rest of the process follows the procedure already described (Fig. 3).

Practical Trials

The injection moulding trials were carried out under conditions as close to practice as possible, i.e. always only in fully automatic operation and with automatic disc removal. The cycle time is between 6 and 12 s, depending on the type of material, the master and the specified injection moulding conditions. In comparison, the cycle time for manufacturing an audio CD today is just under 3 s. All the tests are being carried out on an injection moulding machine of the type Discjet 600 (manufacturer: Netstal, Näfels/Switzerland). The moulding compounds used for the tests were various types of polycarbonate and their copolymers with different melt viscosities and/or different additive contents (e.g. with and without a release agent).

The surface structures differ with regard to the nature and width of the structures, their angle to the direction of flow and their distance from the gating point (Figs. 2 and 11).

For quality control and measurement of the resultant structures, use is made of atomic force microscopy. With this process, a very sharp – ideally, atomically sharp – tip, usually of silicon, scans over the surface. The force with which the tip presses onto the surface is very low, around 1–100 nN. The deflection of the tip is measured by laser reflection, resulting finally in a topographical picture of the surface. Atomic force microscopy allows a resolution down to a range of a few nanometers, depending on the tip and measuring method [5].

Results

To make a comparison of the replication of V-pits with a differing structure width, the aspect ratio is given instead of the structure height. A structure height with an aspect ratio of a = 0.707 thus indicates a 100 % replication of the structure (Fig. 7).

Replication fidelity

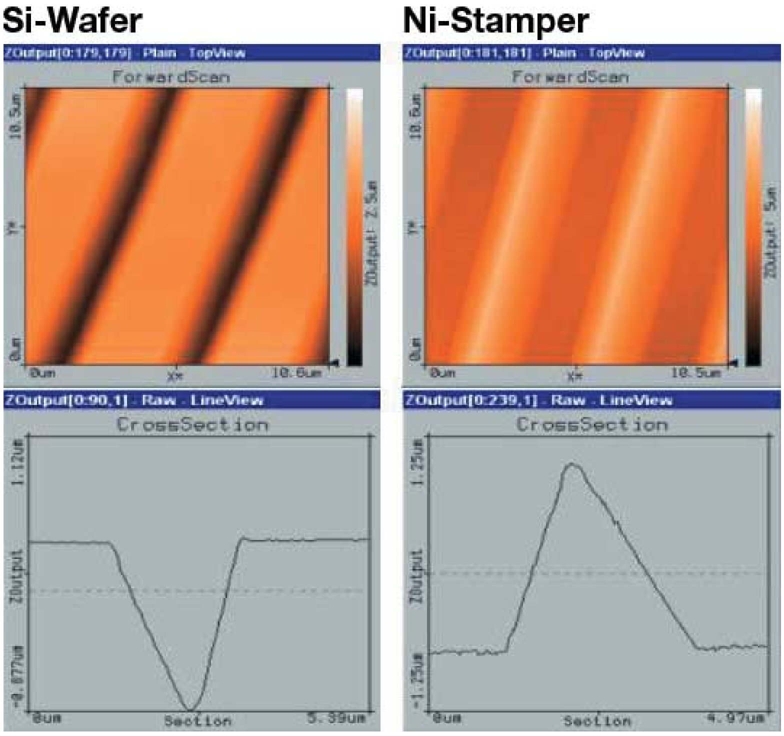

Fig. 6. AFM measurements confirm the high replication fidelity of Ni galvanising

With V-pits, the aspect ratio in the tests was between 0.25 and 0.5. It is also possible to establish a general relationship between replication accuracy and melt viscosity of the various moulding compounds. The lower the viscosity, the better the replication accuracy (Fig. 8). With special materials, this dependency is less evident. In this case, the influence of the viscosity on the replication accuracy seems to be overshadowed by other material properties.

The addition of mould release agents to the moulding compounds produces contradictory results. Release agents are intended to facilitate the process of removing the part from the mould and prevent the plastic sticking to it. They also have to comply with a number of other requirements. For example, they must not affect the properties of the basic polymer, must have excellent compatibility and must not leave deposits on the mould surface [6]. With the moulding compounds investigated here, it was impossible to recognise any clear relationship between the content of release agent and the replication accuracy.

The aspect ratio as a function of the angle between the direction of structure and direction of flow decreases as the angle increases (Figs. 8 and 9).

With the moulding compounds tested in the course of the study, an approximately linear relationship was found – with few exceptions – between the attained aspect ratio and the mould temperature (Fig. 10). At the same time, apart from the mould temperature, other process parameters (such as varying the holding pressure) proved to be of only secondary importance [2].

Positive master structures are fully replicated in plastic (Fig. 11). A simple explanation for the differing replication from positive and negative master structures is the shrinkage behaviour of the plastics. This is similar to the situation observed in thermoforming when using positive and negative moulds.

Outlook

The advancing miniaturisation of structures will remain a key point in the development of optical storage media. The question inevitably arises about the the-

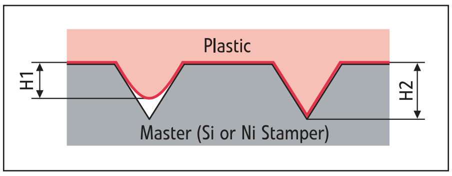

Fig. 7. Schematic diagram of an incompletely replicated V-pit H1 → $a_1 < 0.7070$ (left) and a fully replicated V-pit H2 → $a_2 = 0.707$ (right)

Different moulding compounds

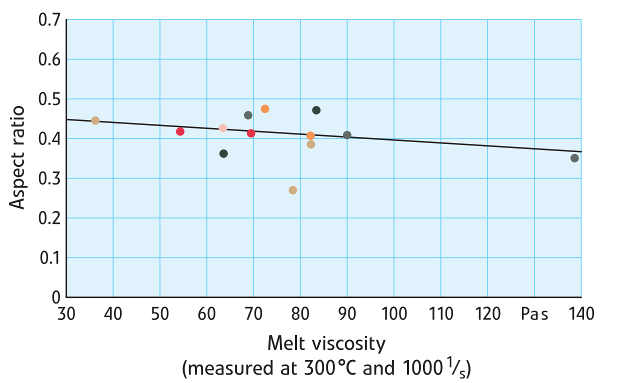

Fig. 8. Aspect ratio as a function of the examined moulding compounds

Dependence on angle

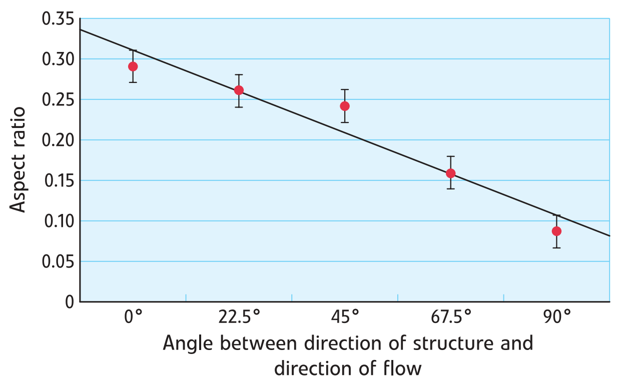

Fig. 9. Results for a polycarbonate at a distance of 25 mm from the gating point and a structure width of 1800 nm

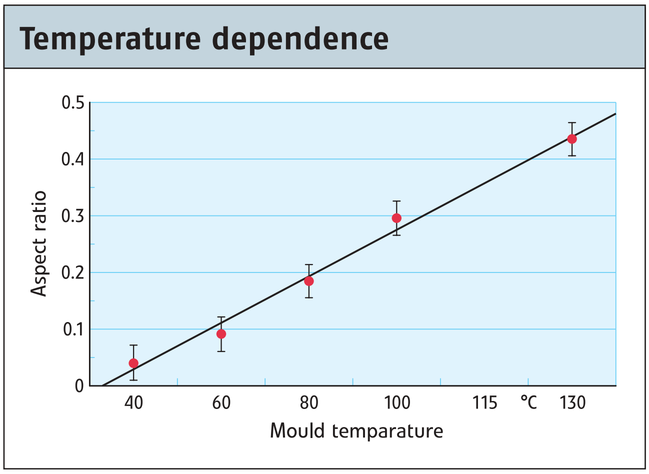

Fig. 10. An approximately linear relationship exists between the attained aspect ratio and the mould temperature for the moulding compounds tested here – with only a few exceptions

oretically smallest possible replication. The results presented here, above all the experience collected in the field of master production, can be seen in this respect as a useful starting basis for further work in this field.

Also important is the question of the stability of such nano structures as a function of time, above all when advancing into even smaller structures. Influences such as temperature, moisture, surface coatings etc. need to be reappraised [7]. As far as the moulding compounds are concerned, the previously measured properties such as glass transition temperature T_g and melt viscosity have probably not yet been determined accurately enough for the nano scale. It may be necessary to state the glass transition temperature as a function of the layer thickness. In addition, further steps should be taken to move from the macro-rheology of the polymer melts to a nano-rheology. ■

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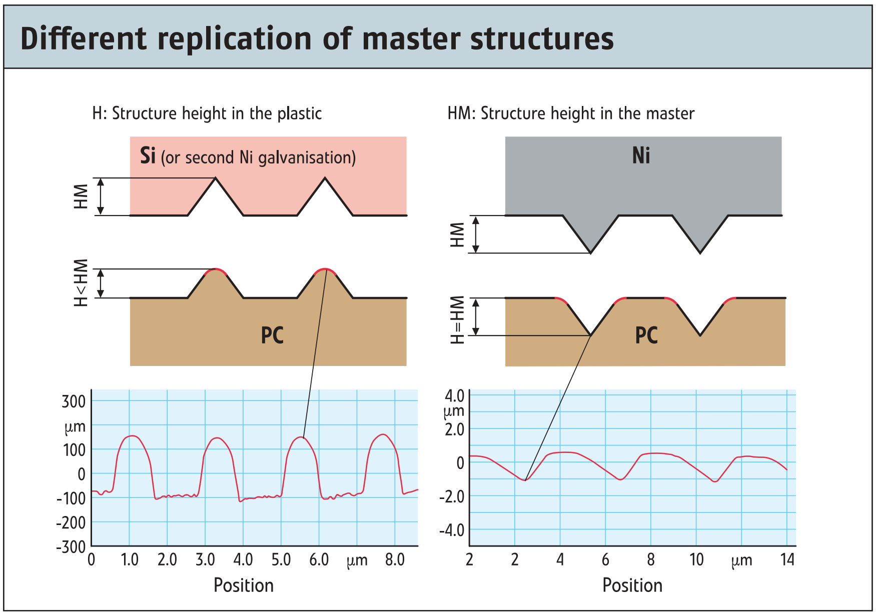

Fig. 11. Comparison of the replication in plastic from negative (left) and positive (right) master structures