Short Communication

Investigation of Liquid Additives on the Nano-Hardness of NiFe during Polishing

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For the optimization of polishing processes, the knowledge of the effectiveness of additives on the surface binding is essential. The nano-hardness was used as an indication for the most adequate acid used as additives. For analyzing the nano-hardness, nanoindentation tests were performed. This paper describes the investigations on the nano-hardness of NiFe affected by hydrochloric acid (HCl) and nitric acid (HNO3) used as liquid additives during a polishing process.

Keywords: tribology, liquid additives, nano indentation, polishing

1. Introduction

In order to prepare a polishing agent for optimizing the surface finishing processes of different materials, the influence of the chemical attack on the surfaces was investigated. Particularly the influence of chemicals on the hardness of surface layers with a depth of a few hundred nanometers occurring on metals like NiFe is of interest and may be used for improving the surface finishing processes. Such a reactive metallic top layer is also affected by mechanical machining processes, which was confirmed by nano indentation studies1). By applying nanoindentation tests, the influence of the polishing agent chemistry on the layer on top of the NiFe layer was investigated. The goal of this work is to create an ultra-smooth surface machining process for thin-films used for Micro Electro-mechanical Systems (MEMS).

2. Experimental investigations

The polishing process used for the investigation is based on Chemical-mechanical polishing (CMP). Figure 1 shows the schematic representation of a CMP tool. The typical application of this process is to minimize the step height between two materials. In this case, this process is used for fabricating ultra-smooth surfaces. To do so, the influence of two acids on a NiFe-layer is investigated.

The machine used for the investigations is shown in Figure 2. It is a dual-axis polishing machine whose polishing plate has a radius of 200 mm.

Figure 1 Schematic representation of a CMP tool

For all experiments, four-inch Si-substrates coated with NiFe were used. The applied contact pressure was 1.5 kPa and the rotational speed of the polishing plate and the wafer holder was 20 rpm.

Figure 2 CMP-machine
3. Investigations on properties of NiFe by nano indentation

For analyzing the hardness and Young’s Modulus of the reactive layers, nano indentation tests were carried out using a Hysitron TriboIndenterTM. For the task, a pyramid-shaped diamond Berkovich tip was used. The tip actuation was provided by the Z-system of the system’s 3D-transducer with a three-plate capacitor as shown in Fig. 3. The indentation depth can be varied from a few ten nanometers up to a few micrometers.

![Fig. 3 Principle of the TriboIndenter™ used for the indentation tests](image)

Loading and unloading curves were created. The curves allow calculating the hardness and Young’s Modulus of the layers by applying the method of Oliver and Pharr2). Additionally to the physical values, the loading and unloading curves were analyzed to gain information on the material behavior as a function of the indentation depth. During the indentation test, the tip may deform the substrate in an elastic, plastic, or elastoplastic way as presented in Fig. 43). The applied load was varied from 0 µN to 1,500 µN.

![Fig. 4 Elastoplastic material properties](image)

4. Influence of chemical attack on the NiFe coated surface

In order to evaluate the influence of mineral acid solutions on the NiFe surface with a composition of 4.26 to 1, etching experiments with hydrochloric acid (HCl) and nitric acid (HNO₃) were performed. The NiFe surfaces were submerged in solutions of the acids with various concentrations (10⁻³ molar to 1 molar) for between one hour and one day. Figure 5 shows an SEM image of an untreated NiFe surface.

![Fig. 5 SEM image of the untreated NiFe surface](image)

After the tests, the NiFe surfaces were subjected to scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) spectroscopy analyses. For concentrations of 0.1 molar or higher, it was found that a complete dissolution of the NiFe layer from the substrate took place. In total, a concentration of 10⁻³ molar and a 3 h treatment were found to be sufficient to achieve an etching of the surface. A distinct increase of the surface roughness can be observed between the SEM images shown in Fig. 5 and Fig. 6.

![Fig. 6 Representative SEM image of the NiFe surface after treatment a) in 10⁻³ molar HCl for 3h, b) in 10⁻³ molar HNO₃ for 3h](image)
Analyzing the SEM images taken after the treatment with either $10^{-3}$ HCl or $10^{-3}$ HNO₃ depicts that both samples show holes and rough structures. The effect is even more pronounced for the sample treated with HNO₃. This is confirmed by results of the EDX analysis. The composition of the NiFe alloy was determined in areas of $10 \mu m \times 10 \mu m$. For the untreated sample of Ni/Fe, this ratio is $3.50 \pm 0.03$, a treatment of Ni/Fe with $10^{-3}$ molar HCl increases it to $4.28 \pm 0.02$ and with $10^{-3}$ molar HNO₃ to $4.35 \pm 0.03$. If the concentration of HCl is increased to 0.2 molar a Ni/Fe ratio of $4.55 \pm 0.03$ is found even if the treatment time is reduced to only 1 h.

The measurements showed a higher Ni content than the expected ratio of 4.26 to 1. The increasing of the Ni/Fe ratio clearly demonstrates that the Fe is more easily dissolved than Ni. The reason is, that the dissolution of a metal in an acid always includes an oxidation at the starting point. Both Ni and Fe are ignoble metals. While the electrochemical potential $E^0$ of Fe for (Fe/Fe²⁺) is -0.44 V. Therefore it is more negative than that the $E^0$ of Ni for (Ni/Ni²⁺), which is -0.23 V. Thus, Fe is easier oxidized than Ni.

Because the oxidation effect of HNO₃ is higher than that of HCl, the observed surface roughness after the treatment with HNO₃ as well as the Ni/Fe ratio was higher than with HCl.

Exemplarily for Fe the reaction equation is:

$$Fe + HNO_3 \rightarrow Fe^{2+} + NO_2^- + OH^- \quad (1)$$

For both acids, the changes in the Ni/Fe ratio are quite high and a concentration of above 0.1 molar results in a complete dissolution after a short time. This indicates, that the used concentrations and treatment times can be drastically shortened for a real polish process.

The influence of the chemical attack on the hardness of NiFe surfaces was analyzed by indentation tests. Figure 7 presents the loading and unloading curve for samples exposed to a $10^{-3}$ molar solution of HCl or HNO₃, respectively. Both etchants created a surface layer on top of the NiFe with a thickness of 400 nm and a substantially reduced hardness of 2 GPa.

A load of 200 $\mu$N resulted in a maximal indentation depth of 50 nm and a hardness of 2 GPa. The indentation shows different results in relation to the elastoplastic behavior.

5. Tribochemical experiments

For the tribochemical investigations, three different fluids were chosen for the polishing process. The first one is DI water which is used as reference. For the second and third run $10^{-3}$ molar HCl and $10^{-3}$ molar HNO₃ were applied. Three samples in each test were used, each one was subjected to a CMP process with water for three different lengths: 5 min, 10 min, and 15 min. Each sample was characterized on a load of 200 $\mu$N, 500 $\mu$N, and 1,500 $\mu$N. Figure 8 shows an example of the hardness in the nano indentations with a force of 1,500 $\mu$N after the polishing process with water. The value of the hardness of each sample independent on the process time with water was 6.55 GPa.

The investigations for the polishing tests with the considered acids are shown in more detail. Examples for the indentations are presented in Figure 9. These samples were subjected to a CMP process with an HCl liquid for 5 min.
Figure 9 shows the typical loading-unloading curves of the measurements with the Hysitron NanoIndenter™. The test conditions mentioned before (CMP process time: 5 min, 10 min, and 15 min) were also used for the experiments with HCl and HNO₃. The indentations were done with the same forces as mentioned above. Figure 10 presents a summary of all measurements.

The results of the tribochemically machined experiments with HCl show that the hardness is independent of the process time. The results for the experiments with HCl and HNO₃. The indentations were done with the same forces as mentioned above. Figure 10 presents a summary of all measurements.

Fig. 10 Summary of the results achieved with HCl

The results of the tribochemically machined experiments with HCl show that the hardness is independent of the process time. The results for the investigations with HNO₃ are summarized in the following (Figure 11).

Fig. 11 Summary of the results achieved with HNO₃

The tribochemical machining experiments with HNO₃ show a dependence on the process time. The emerging surface is hardened by the planarization process. Finally, the polished and unpolished surfaces are compared (Fig. 12).

Fig. 12 Indentation Results for etched and tribochemically machined NiFe surfaces a) treated with HCl, b) treated with HNO₃.

The etched unpolished surface is less hard than the tribochemically machined surface. This effect can be attributed to an abrasion of the etched NiFe substrates and a compacting of the surface during the CMP process, which is caused by the pressure.

6. Conclusion and outlook

The results of the investigations show the influence of acids on NiFe surfaces during the polishing process. The change of the hardness is an important factor for optimizing polishing fluids for the surface finishing process. The knowledge of the acid influence is very useful for optimizing the surface finishing process. Ultimately, an optimum between the Young’s Modulus (which can also be derived from the nano indentation data), the cutting rate, and the surface finish has to be found.

7. References