Quantitative analysis of the frictional properties of solid materials at low loads. II. Mica and germanium sulfide

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Load-dependent studies of the frictional properties of mica and germanium sulfide were performed by friction force spectroscopy in air and in argon atmosphere. Well-defined spherical tips made from amorphous carbon were used to profile the surface at low loads. In air, the frictional force F_f as a function of the normal force F_n for GeS follows an $F_f \sim F_n^{2/3}$ behavior with good agreement, as is predicted by contact mechanical theories for a Hertz-type contact with small tip radius, with not too soft tip and sample materials, and with low surface energies involved. The friction of mica, however, deviates significantly in many cases from the $F_f \sim F_n^{2/3}$ law due to its higher surface energy. In argon, chemical reactions between clean sample and tip material prevent the observation of wearless friction on *in situ* prepared samples. These effects were partially suppressed by an *ex situ* cleavage of the mica or germanium sulfide samples. [S0163-1829(97)00335-4]

I. INTRODUCTION

In Part I of this paper,[1] we have demonstrated by the analysis of the nanotribological properties of different carbon compounds that the frictional force F_f per unit area A (the so-called shear stress S) is *independent* of the mean contact pressure $p = F_n/A$ at normal forces F_n where no wear occurs, and that contact mechanical methods are under certain conditions excellently suited to describe the elastic deformation of a tip with spherical apex on a flat sample surface even if the radius of the tip apex is in the range of some nanometers. Additionally, we have shown that the friction coefficient $\mu = F_f/F_n$ is not well suited for comparing the tribological behavior of different materials in the case of single-asperity friction. Therefore, we introduced an effective friction coefficient for point-contact-like single-asperity friction $\widetilde{C}$ for the classification of the microscopic frictional properties of solid materials.

Starting from these results, we will analyze in this paper the frictional properties of muscovite mica and germanium sulfide under ambient conditions as well as in an oxygen-free and water-free argon atmosphere using the theory and the experimental procedure presented in Part I. Similarities and differences between the frictional behavior of mica, germanium sulfide, and the carbon compounds will be discussed.

II. EXPERIMENT

The friction of mica is of considerable interest since it possesses a well-defined lamella structure. This leads, after cleavage, to individual molecularly flat terraces at the surface that can be extraordinarily large: terraces of thousands of μm^2 and more are common. For this reason, the frictional properties of mica are well studied with the surface force apparatus, where it is used as a substrate for lubricating thin films (see, e.g., Ref. 2). For the friction force microscope, there are also a number of studies where the friction coefficient of mica was measured under different conditions.[3–7] In these

studies, friction coefficients between 0.05 and 0.3 were observed, depending on the relative humidity of the surrounding atmosphere.[7] However, force spectroscopy measurements in argon atmosphere with a water and oxygen content below 1 ppm have not been reported yet.

GeS is also a layered material which can easily be cleaved along its (001) plane using Scotch tape. This allows, similar to mica, an easy preparation of clean surfaces prior to measurement. The crystal exhibits atomically smooth terraces of typically some μm^2 size. An extensive discussion of the surface structure of GeS and typical force micrographs can be found in Ref. 8. GeS has been of interest because of its outstanding properties as substrate for the layer-by-layer growth of epitaxial, single-crystalline C_{60} thin films. A high friction coefficient of $\mu \approx 1.5$ was found for GeS.[9]

The scanning and friction force spectroscopy investigation was performed at room temperature both under ambient conditions and in a water-free and oxygen-free argon atmosphere. Measurements were carried out using the same specially prepared tips with well-defined spherical tip ends and known tip radii and the identical experimental setup as already described in Part I.[1] Additionally, the definitions of the parameters and coefficients used below and the equations used for data analysis and curve fitting are also given in Part I.

III. RESULTS

Figure 1 shows a plot of the frictional force F_f versus the normal force F_n acquired on a freshly cleaved germanium sulfide crystal in air. The friction was found to be very high, in agreement with the results of Ref. 9. At a normal force of 10 nN, e.g., we already detected a frictional force of nearly 20 nN. For the present measurement, a tip with an apex radius of $R = (20 \pm 5)$ nm was used, $n = 134$ data points were taken, and an adhesion of $F_0 = 11.0$ nN was obtained. The fit according to Eq. (12) of Part I shows good agree-
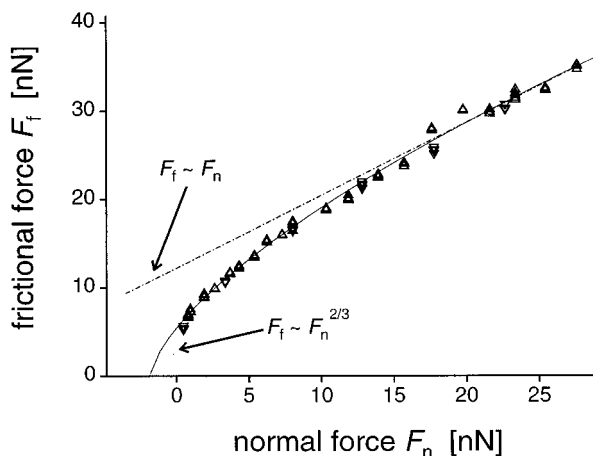
FIG. 1. The frictional force F_f as a function of the normal force F_n, measured on a freshly cleaved GeS(001) surface in air. The experimental data show good agreement with the $F_f \sim F_m^{2/3}$ law according to Eq. (12) given in Part I (Ref. 1) and cannot be described by a linear $F_f(F_n)$ dependence (see the fit curves displayed in the plot). A tip with an apex radius of $R = (20 \pm 5)$ nm was used for the measurement; $n = 134$ individual data points are displayed. The adhesion F_0 was 11.0 nN, $\widetilde{C}$, and F_{off} were calculated to $\widetilde{C} = (0.50 \pm 0.21)$ nN$^{1/3}$ nm$^{-2/3}$ and $F_{off} = -1.8$ nN.

ment between theory and experiment. Values of $\widetilde{C} = (0.50 \pm 0.21)$ nN$^{1/3}$ nm$^{-2/3}$ and $F_{off} = -1.8$ nN (which fulfills the condition $|F_{off}| \ll |F_0|$ introduced in Part I) were calculated.

Under ambient conditions, a total of 32 $F_f(F_n)$ data sets were acquired using five different tips. In most cases, a non-linear dependence of the frictional force on the normal force was found that was very close to the predicted $F_f \sim F_n^{2/3}$ dependence. Averaging all measurements leads to a mean value for $\widetilde{C}$ of (0.328 ± 0.128) nN$^{1/3}$ nm$^{-2/3}$.

A typical $F_f(F_n)$ curve acquired in air on mica is shown

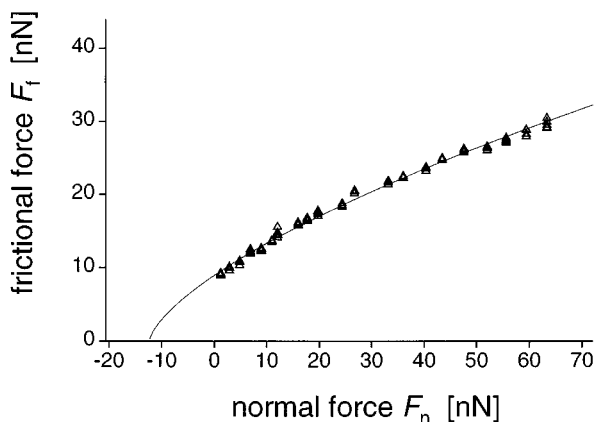
FIG. 2. $F_f(F_n)$ plot for mica. The corresponding measurement was carried out on a freshly cleaved sample in ambient air. The calculated $\widetilde{C}$ is (0.14 ± 0.05) nN$^{1/3}$ nm$^{-2/3}$, which is significantly lower than the value derived in Fig. 1 for germanium sulfide. Note the large offset of the frictional force at $F_n = 0$ nN. The relevant parameters of the measurement are given in the text.

in Fig. 2. A tip with an apex radius of $R = (47 \pm 3)$ nm was used, 135 data points were taken. The adhesion F_0 was 55 nN. $\widetilde{C}$ was calculated to (0.14 ± 0.05) nN$^{1/3}$ nm$^{-2/3}$, and an offset force $F_{off} = -12.3$ nN was found. This value of $\widetilde{C}$ is in excellent agreement with the mean value for $\widetilde{C}$ of (0.139 ± 0.056) nN$^{1/3}$ nm$^{-2/3}$, which was derived by averaging a total of ten measurements performed with four different tips.

In the case of mica investigated in air, it was remarkable that often significant frictional forces were measured at $F_n \approx 0$ nN, causing quite large calculated values for F_{off} when compared with the observed adhesion. Additionally, about one-third of the acquired data sets show significant deviations from the expected $F_f \sim F_n^m$ law with $m = 2/3$, where deviations with $m > 2/3$ as well as $m < 2/3$ occurred.

Freshly cleaved mica has a very high surface energy of 600 mJ/m^2 due to positively charged K$^+$ ions at its surface.[10] Under ambient conditions, molecules from the atmosphere are attracted to the surface, where they form a contamination layer in order to reduce the surface energy of the system. In dry argon, however, the surface charges cannot be compensated. Therefore, strong long-range electrostatic forces are acting between tip and sample in argon that prevent a controlled approach of the tip to the sample surface in our experiments and lead to extraordinary large jump-in peaks. After making contact, the charges can compensate, leading to a reduction of the attractive tip/sample forces and eventually causing a jump off of the tip from the surface. Thus, a reliable determination of the effective acting normal force was impossible. Moreover, a chemical reaction occurred at the tip/sample interface that manifested itself in gradually appearing surface features in the simultaneously acquired topographical information on formerly molecularly flat surface regions, and in a truncation of the tips observed in control measurements carried out after performing force spectroscopy on mica in argon atmosphere.[11]

For these reasons, no meaningful spectroscopical data could be obtained on mica cleaved in argon atmosphere. By cleaving in air with subsequent transfer into the argon chamber, we tried to examine the influence of the water film on the measured friction. Samples prepared in such a way could be successfully measured in most cases. The shapes of the curves acquired under these conditions were quite close to the expected $F_f \sim F_n^{2/3}$ dependence [see, e.g., the $F_f(F_n)$ plot displayed in Fig. 3]; the numerical values extracted for $\widetilde{C}$, however, varied in an unacceptable wide range, and sometimes large forces F_{off} occurred. Therefore, we cannot make any reasonable quantitative statements about the friction of mica under these conditions.

Similar problems also occurred for GeS in argon. If the GeS single crystals were cleaved *in situ*, chemical reactions at the tip/sample interface prevented the acquisition of meaningful force spectroscopical data. Samples that were cleaved *ex situ* and introduced into the argon chamber about 5 min after cleaving surprisingly exhibited a nearly linear dependence of the frictional force on the normal force and sometimes a very high friction for normal forces close to $F_n = 0$ nN even for small tip radii (see Fig. 4). Additionally, an increased wear of the tip apex could be confirmed.
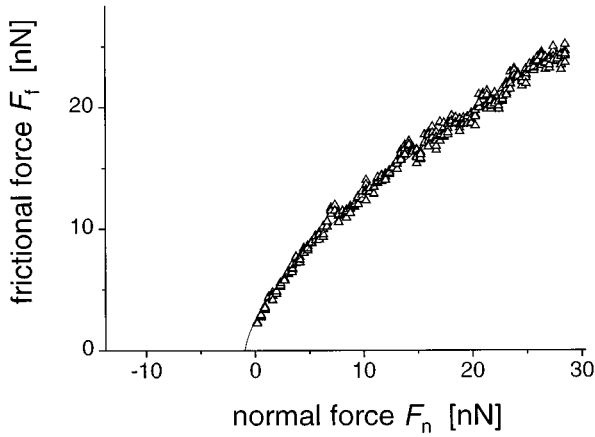
FIG. 3. $F_f(F_n)$ plot for mica. The corresponding measurement was performed in argon atmosphere on a sample that was cleaved under ambient conditions about 5 min before introducing it into the argon chamber. For the measurement, a tip with a radius of $R = (67 \pm 9)$ nm was used, $n = 400$ data points were taken, and an adhesion of $F_0 = 14.9$ nN was detected. Data analysis leads to $\widetilde{C} = (0.16 \pm 0.04)$ nN$^{1/3}$ nm$^{-2/3}$ and $F_{off} = -0.8$ nN.

IV. DISCUSSION

It was found that the tribological behavior of mica and germanium sulfide deviated in several ways from the behavior of the carbon compounds found in Part I.[1] Possible origins for these differences will be discussed in the following.

We have seen that both materials react with the tip material if they are cleaved in argon. Hence, the conditions for wearless friction were not fulfilled. If the samples were cleaved under ambient conditions with subsequent transfer into the argon chamber some minutes after the cleavage, measurements without the obvious occurrence of wear were possible in the case of mica. The formation of an adsorption layer which protects and stabilizes the sample surface could be the reason for this 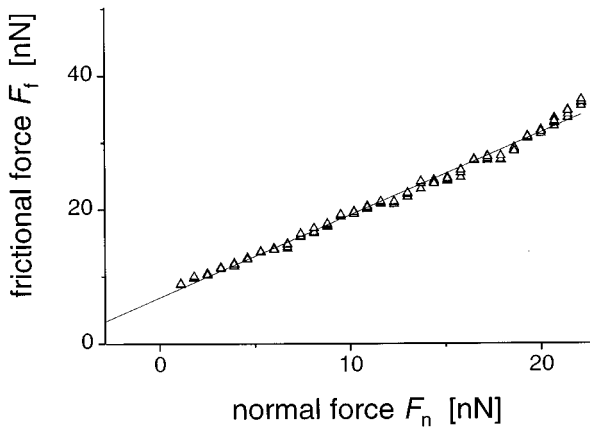behavior; the formation of such an adsorption layer that is stable even in dry argon in order to compensate the positive charges from the K$^+$ ions is likely (see Sec. III). The measurements, however, were not sufficiently reproducible, which is probably due to variations in thickness and composition of the adsorption layer.

On the other hand, the surface of germanium sulfide has no free charges at the top; hence, its surface energy will be lower, resulting in a nonstable surface adsorption layer unlike the case of mica. The layer of adsorbed molecules that remains on the GeS surface in argon cannot sufficiently prevent chemical reactions between tip and sample, explaining the occasional high offset at $F_n = 0$ nN and the increased wear of the tip apex. Therefore, the conditions for wearless friction are again not fulfilled. The linear dependence of the $F_f(F_n)$ data indicates that the tip end flattens and that the contact changes from single-asperity to multiasperity sliding or that debris particles are present in the tip/sample contact.

Measurements carried out under ambient conditions were successful for both GeS and mica; the thick adsorption layers that are always present in air can obviously sufficiently passivate the sample surface in order to prevent chemical reactions between tip and sample. However, in the case of mica, significant deviations from the 2/3 power law of some $F_f(F_n)$ curves were observed, whereas the $F_f(F_n)$ curves obtained on GeS were in most cases quite close to the 2/3 power law. This can be understood based on the calculation of the surface energy γ. If $\Phi < 0.1$ [Eq. (6) in Part I], Bradley[12] and Derjaguin, Muller, and Toporov[13,14] have shown that the surface energy γ can then be calculated from the adhesion force F_0 by the simple equation $\gamma = F_0 / 4 \pi R$. This leads with the adhesion force F_0 taken from the data presented in Fig. 1 to $\gamma = 11 \times 10^{-9} / 4 \pi (20 \times 10^{-9})$ J/m^2 $= 44$ mJ/m^2. With this value for γ and $R = 20$ nm, $z_0 = 3$ Å and $K \approx 50$ GPa (exact values for the elastic parameters of the tip as well as the sample are not available), Φ is calculated to 0.11. Hence, Eqs. (8), (9), and (10) given in Part I should apply. In the case of the mica data from Fig. 2, γ is calculated to 93 mJ/m^2, leading to $\Phi = 0.24$. This is already outside the range for which Eqs. (8)–(10) are good approximations since Φ is significantly larger than 0.1. Therefore, more sophisticated mathematical models than the one introduced above have to be applied for a better description.[9,15–17]

As a result of this discussion, we would like to point out that it is not possible to measure wearless friction between an amorphous carbon tip and a clean mica or GeS surface, respectively, due to the occurrence of chemical reactions. Wearless friction between tip and sample is always strongly influenced by the properties of the adsorption layers which passivate and lubricate the sample as well as the tip surface.

V. CONCLUSION

To summarize, we presented load-dependent measurements of the frictional force obtained on mica and germanium sulfide. Well-defined, approximately pointlike single-asperity tips made from amorphous carbon were used for the experiments performed in argon as well as in air at low loads. It was shown that chemical reactions prevented the observation of wearless friction on clean surfaces in dry argon. The existence of an adsorption layer due to a sample preparation under ambient conditions could partially sup-

FIG. 4. $F_f(F_n)$ plot for GeS measured in argon atmosphere. The tip radius R was (13 ± 2) nm, $n = 161$ data points are displayed, and the adhesion was $F_0 = 14.4$ nm. The data follow a linear $F_f(F_n)$ dependence; a friction coefficient of $\mu = 1.22 \pm 0.40$ can be calculated. Note the high offset of $F_f \approx 8$ nN at $F_n = 0$ nN.

press these reactions. In air, the friction of GeS follows in good agreement an $F_f \sim F_n^{2/3}$ behavior, as predicted for a Hertz-type contact with $\Phi \approx 0.1$ or smaller. The friction of mica, however, deviates in many cases significantly from the $F_f \sim F_n^{2/3}$ law due to the higher surface energy of the material, which increases the parameter Φ significantly over the value of 0.1. Therefore, more comprehensive contact mechanical theories should be applied for a precise description of the $F_f(F_n)$ dependence of mica.

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