A dispersive multilayer interference mirror with a group delay dispersion (GDD) of $+1500 \text{ fs}^2$ for the spectral range of 9–11.5 $\mu$m is presented. It is designed to compensate the GDD of an ultrashort light pulse gained when transmitting 1 mm of a zinc selenide substrate. The coating process for the mirror manufacturing is described. The optical properties of the mirror are fully characterized by measuring the group delay, the GDD, the reflectance, and the transmittance.

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1. INTRODUCTION

A laser source generating high-power ultrashort light pulses in the mid-infrared (MIR) spectral region of 6.8–16.4 $\mu$m and with an average power of 0.1 W was recently developed [1]. Such coherent broadband lasers are indispensable for highly sensitive mid-infrared spectroscopy for applications like quality control, forensic analysis, and biomedical research [2–4]. A key reason for advancing this new technology involves the availability of mid-infrared dispersive mirrors (also known as “chirped” mirrors) [5–9], which allow for the efficient generation and manipulation of broadband few-femtosecond mid-infrared pulses.

Here, for the first time, to the best of our knowledge, we report on the development of a mid-infrared broadband dispersive mirror with a group delay dispersion (GDD) of $+1500 \text{ fs}^2$ on average and a bandwidth of 9–11.5 $\mu$m. The coating process for MIR interference coatings is described in detail. Germanium (Ge) as the coating material with a high refractive index and zinc sulfide (ZnS) as the low-index material are employed.

2. COATING PROCESS

The choice of coating material is crucial for the MIR range. Here we present some of our considerations. Zinc sulfide (ZnS) has a refractive index of about 2.2 at 2 $\mu$m and is used as a low-index material with germanium. It can also be used as a high-index material in combination with fluoride materials, which have a refractive index of around 1.5. Zinc sulfide with grains of 1.5–5 mm and a purity of 99.99% was employed. The process temperature is set to a rather low value of 80°C because the zinc sulfide layer thicknesses become more sensitive with increasing process temperatures. The reason for this is that zinc sulfide totally dissociates during evaporation, and the condensation coefficient of Zn rapidly decreases with increasing substrate temperatures [10]. Therefore, the deposition rate decreases significantly at higher temperatures and more material accumulates on the chamber walls. The effect was observed by coating zinc sulfide single layers onto a germanium and fused silica substrate in one coating run. Since the fused silica substrate absorbs more infrared radiation of the heaters, the layers were about 3% thinner than on the germanium substrate, which mostly transmits heat radiation and stays cooler. The search for a good process to evaporate zinc sulfide required many attempts. Only a few process details for zinc sulfide can be found in the literature [10–16].

For our process, zinc sulfide is evaporated using electron-beam (e-beam) deposition, with the coating plant Syrus pro 710 (Leybold Optics GmbH, Germany). A so-called ring-rill crucible is used with a volume of 250 cm$^3$. The ring-rill crucible slowly rotates with 0.1 rounds per min, while the e-beam sweeps only one small radial stripe of zinc sulfide. A current of the electron beam of 20 mA yields a deposition rate of about 1.0 nm/s. It was found that zinc sulfide single layers have adhesion problems on most of the employed types of substrate materials. Thicker layers of about more than about 500 nm did not pass a tape test, where the adhesion of the coating is tested by trying to pull it off with adhesive tape. The solution for this problem was found by coating a thin germanium layer on the substrate before the zinc sulfide. The dispersive
multilayer coating described below is made with germanium as the first layer and shows excellent adhesion.

Since the coating plant is equipped with an in situ broad band monitor for the visible and near-infrared spectral range, it was possible to measure the vacuum shift of the zinc sulfide layers. A spectrum is measured in vacuum after the coating process, and another one is taken after venting the chamber. After one hour in atmosphere, the spectrum shifted only about 1%. This indicates a dense and optically stable layer structure. Since germanium is not transparent in the working range of the optical monitoring system, no direct information on the vacuum shift was obtained. However, we still assume that the germanium layers are very dense because none of the deposited multilayer coatings exhibited a water-absorption peak around the wavelength of 3 μm, as is well-known for the porous fluoride materials like, for instance, lanthanum fluoride.

Germanium is used as a high-index material with its high refractive index of 4.1 at a wavelength of 5 μm. As for zinc sulfide, only a few process details are published for germanium [11,12,15,17]. In this work, germanium is only used in combination with zinc sulfide. Therefore, the temperature is also set to 80°C. The raw germanium consists of grains with sizes of 1–3 mm and a purity of 99.999%. Also, a large amount of germanium is needed to realize MIR dispersive mirrors. Therefore, a copper crucible with five pockets is used. Each pocket can hold germanium with a volume of about 38 cm³. Germanium is filled directly in the copper pocket. It was found that germanium seems to not react with copper since the molten germanium block can easily be removed from the pocket by hands; it does not stick to the copper. The pocket is filled up with material within several time-consuming steps. Germanium granulate is filled to about one third of the pocket. Then it is molten under vacuum until no grains are left and a solid block of germanium is created. This is repeated until the pocket is full with germanium. If one fills the whole pocket with granulate at once, molten germanium is built at first only at the surface and seals the grains underneath. The residual contaminations like water on the grains evaporate and blow up the molten germanium. For the multilayer coating process, the germanium block made as described above, builds a stable melt and allows a steady deposition rate of 0.5 nm/s.

With the process parameters mentioned above, single layers of zinc sulfide and germanium are deposited on potassium bromide (KBr) substrates, which have a low refractive index of 1.5 at a wavelength of 10 μm and are highly transparent from 0.4 to 20 μm. The KBr substrates were suitable for the single layers but suffered from bad adhesion of multilayer stacks, even when germanium was used as the first layer. The thickness of the zinc sulfide single layer was about 500 nm, and no layer for adhesion promotion was used. The transmittance of the coated substrates is measured using a FTIR spectrometer (Vertex 70 from Bruker Optik GmbH, Germany). The single-layer spectra were evaluated using the software OptiChar (Optilayer GmbH, Germany). The Sellmeier model for the dispersion of the refractive index was used to fit the measured spectra. The formula is

\[ n^2(λ) = A_0 + \frac{A_1 λ^2}{λ^2 - A_2} + \frac{A_3 λ^2}{λ^2 - A_4}. \]

<table>
<thead>
<tr>
<th>Material</th>
<th>A₀</th>
<th>A₁</th>
<th>A₂ [μm²]</th>
<th>A₃</th>
<th>A₄ [μm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>18.50</td>
<td>-2.014</td>
<td>-11.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnS</td>
<td>5.312</td>
<td>-0.359</td>
<td>-3.884</td>
<td>0.508</td>
<td>461.9</td>
</tr>
</tbody>
</table>

The according Sellmeier coefficients for wavelengths in micrometers are given in Table 1. For the data evaluation, the range of 2–12 μm was used. Thus, for this range, the coefficients are valid.

Germanium requires three coefficients of the equation to sufficiently describe the dispersion. Zinc sulfide requires five coefficients to map the turning point of the dispersion at the wavelength of about 6 μm. The existence of this turning point can also be seen in [18,19].

3. DISPERSE MIRROR

The dispersive mirror is designed to have an average GDD of +1500 fs² for the bandwidth of 9–11.5 μm. For the calculations, the software OptiLayer was used (Optilayer GmbH, Germany). The amount of GDD is capable of compensating the dispersion of 1 mm zinc selenide. For this first approach, the third order dispersion (TOD) of zinc selenide was neglected, resulting in a constant GDD target value of +1500 fs². The coating design of the dispersive mirror is given in Fig. 1.

The first layer is germanium to improve the adhesion as described above. The design has 36 layers and a total physical thickness of 30.7 μm. This enormous thickness exceeds the thickness of conventional near-infrared dispersive mirrors of more than a factor of two [20]. Both materials are evaporated with the process described above, and all of the four available quartz crystals in the crystal changer were prepared. The crystal is changed after depositing around 8 μm of coating material.

A germanium and a zinc selenide (ZnSe) substrate were coated with the fully automated process. After the coating process, the adhesion of the coating was tested with a tape as described above. The coating was not removed by the tape and therefore passed the test.

4. CHARACTERIZATION

The coated mirrors are characterized by measuring the transmittance and reflectance spectra using the FTIR spectrometer.

![Fig. 1. Layer thicknesses of the dispersive mirror. Layer number 1 is on the substrate and number 36 is exposed to air, from where the laser pulse is incident.](image-url)
mentioned above. The measurements show that the mirror is spectrally shifted to longer wavelengths by 4%. This shift is a manufacturing tolerance and is caused by not yet correct tooling factors of the layer thickness measuring quartz crystals. The shift is added to all following theoretical design curves to allow better comparison with the measurements.

For absolute reflectance measurements, a “V-W” accessory for the FTIR spectrometer is employed. The results are in Fig. 2. It shows the reflectance and the transmittance of the mirror. As a reference for the reflectance measurement, a gold mirror was also measured. With the given values, the absorption is calculated by \( A = 100\% \cdot T \cdot R \), assuming that there is no scattering. The absorption is 3% on average for the reflectance band. Reverse engineering was conducted on the measurements shown in Fig. 2 to estimate the extinction coefficient, which could explain the absorption.

The result is that either zinc sulfide or germanium has an extinction coefficient of about \( k = 1 \times 10^{-2} \). This value could also be caused by both materials in sum. In Ref. [21], an extinction coefficient is published of \( k = 1 \times 10^{-2} \) for germanium and \( k = 1 \times 10^{-3} \) for zinc sulfide [22]. Thus, the observed absorption is likely induced by germanium.

For measuring the group delay (GD) and GDD, a recently published white light interferometer (WLI) for the mid-infrared spectral region is employed [23] (Fig. 3). A WLI is basically a Michelson interferometer operated with a broadband light source [24–26]. The output signal from the interferometer is measured with the same FTIR spectrometer described above. This is enabled by the external input of the device. The path length of one interferometer arm is changed by a motorized stage. After each 100 nm, a spectrum is acquired until 4000 spectra are reached. With this method, interferograms for all measured wavelengths are produced, and their envelopes are computed. The relative delay of the envelope for two different wavelengths yield directly the GD, and its derivation in frequency space gives the GDD. To reduce noise in the results, smoothing was applied by calculating the moving average. The results of the dispersive mirror are given in Fig. 4. The measurement is in good agreement with the theoretical values.

5. CONCLUSION
We demonstrate for the first time, to the best of our knowledge, a mid-infrared dispersive mirror. The coating process requirements and parameters for the two coating materials germanium and zinc sulfide are described in detail, and the indispensable GDD measurement for ultrafast applications is shown. With this coating process and its characterization, the potential of realizing also other kinds of mid-infrared dispersive mirrors is given. These new possibilities pave the way for advancing the development of femtosecond mid-infrared lasers by manufacturing customized dispersive mirrors for a precise dispersion management.

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