Resonant bonding in crystalline phase-change materials

KOSTIANTYN SHPORTKO1, STEPHAN KREMERS1, MICHAEL WODA1, DOMINIC LENCER1, JOHN ROBERTSON2 AND MATTHIAS WUTTIG1,3*

1Institute of Physics (IA), RWTH Aachen University, 52056 Aachen, Germany
2Engineering Department, Cambridge University, Cambridge CB2 1PZ, UK
3JARA-FIT, RWTH Aachen University, 52056 Aachen, Germany
*e-mail: wuttig@physik.rwth-aachen.de

The identification of materials suitable for non-volatile phase-change memory applications is driven by the need to find materials with tailored properties for different technological applications and the desire to understand the scientific basis for their unique properties. Here, we report the observation of a distinctive and characteristic feature of phase-change materials. Measurements of the dielectric function in the energy range from 0.025 to 3 eV reveal that the optical dielectric constant is 70–200% larger for the crystalline than the amorphous phases. This difference is attributed to a significant change in bonding between the two phases. The optical dielectric constant of the amorphous phases is that expected of a covalent semiconductor, whereas that of the crystalline phases is strongly enhanced by resonant bonding effects. The quantification of these is enabled by measurements of the electronic polarizability. As this bonding in the crystalline state is a unique fingerprint for phase-change materials, a simple scheme to identify and characterize potential phase-change materials emerges.

Phase-change materials are solids characterized by an unconventional combination of properties. The amorphous and crystalline phases of these materials possess significantly different optical properties. At the same time, these alloys can be rapidly switched between both states. Such characteristics are ideally suited for applications in rewritable optical data storage. Up to now, three different generations of optical storage media use phase-change materials for rewritable data storage. In compact discs, a 780 nm wavelength laser (1.59 eV) is used to read, write and erase the data. In second- and third-generation products, this wavelength is reduced to increase storage density. In DVDs, a wavelength of 650 nm (1.91 eV) is used, whereas in Blu-ray discs, a wavelength of 405 nm (3.06 eV) is used. As the bandgap of typical phase-change materials is well below 1.5 eV, these optical excitations cause band-to-band transitions.

A second application is in electronic phase-change memory, which uses the pronounced difference in resistivity between the phases. This is a non-volatile memory that has fast data transfer rates and high storage densities. It could enable phase-change memory to replace flash memory in the future and has the potential to create a ‘universal memory’ that might compete with the speed of dynamic random access memory. A number of material properties are critical for this application, including the resistance contrast, transition speed between amorphous and crystalline state and material dependence of the switching characteristics. These are again ultimately related to the materials’ electronic states.

Here, we investigate the dielectric function \( \varepsilon(\omega) \) of each phase by infrared spectroscopy and spectroscopic ellipsometry. The present study focuses on the energy range above the highest phonon frequencies (30 meV) but below the optical gap of typically 0.75 eV. In this range, the dielectric function \( \varepsilon(\omega) \) is governed by the electronic polarizability of the valence electrons, and probes the chemical bonding of the phase-change materials. This enables us to give an unambiguous interpretation of the difference between the bonding in the amorphous and crystalline state. It shows that the bonding in the crystalline phase is unusual in its large component of resonant bonding.

The sample geometry shown in Fig. 1 was used to determine the dielectric function. The reference specimen, shown in Fig. 1a, consists of a glass substrate coated with a 150 nm Au layer, which acts as an almost ideal mirror in our energy range. Films of different stoichiometry were then sputter-deposited on top of this layer, and the reflectance of the samples determined. Phase-change materials such as GeTe, GeSbTe, GeSbTe, GeSbTe, GeSbTe, GeSbTe, and AgInSbTe were used, and compared with conventional \( sp^3 \)-bonded semiconductors such as AgInTe. The sample geometry in Fig. 1b ensures that the measured reflectance spectra are exclusively governed by the dielectric function \( \varepsilon(\omega) \) of the film and its thickness. As the materials investigated are either amorphous or polycrystalline and have no pronounced texture, \( \varepsilon(\omega) \) is isotropic. Our method contrasts with previous studies that focused on higher energies or used Fourier-transform infrared spectroscopy (FTIR) in transmittance mode, which hinders the separation of changes in thickness and optical properties.

Figure 2 shows infrared reflectance measurements for the amorphous and crystalline phases of a typical non-phase-change material, AgInTe. The blue curves are the reflectance spectrum of a 0.65 ± 0.01-µm-thick film of as-deposited AgInTe, confirmed to be amorphous by X-ray diffraction. The film was annealed for 30 min at 180°C, which crystallized it to a four-fold-coordinated...
There are three significant differences between the amorphous and crystalline curves. These are also denoted in the figure. First, the interference fringes extend to much higher photon energies for the amorphous than the crystalline phase, owing to the larger bandgap of the amorphous phase. Second, the reflectance maxima are lower in the crystalline phase, owing to subgap (Drude-like) absorption by free carriers. Third, and most important, is the pronounced difference in spacing of the reflectance minima. The spacing is about 40% smaller in the crystalline phase, which added to the thickness difference, implies that the refractive index is ~50% larger in the crystalline phase. This is supported by a detailed analysis of the spectra in Fig. 4a–d, which show both the real and imaginary part of the dielectric function, that is, \( n \) and \( \varepsilon \).

The reflectance spectra of all investigated phase-change materials show a similar effect; \( \varepsilon_\infty \) is much larger in their crystalline phase. This is also visible in the two extra measurements shown in the Supplementary Information, and was also noted by Mendoza-Galvan and Gonzalez-Hernandez. As can be seen from Fig. 4a–d, the excess of \( \varepsilon_\infty \) for the crystalline phase is significant and reaches values over 200%. This difference is a generic feature of phase-change materials. Whereas the spectra of the amorphous phases resemble that of amorphous AgInTe, the crystalline spectra show a distinct difference. This is clear evidence for a difference in bonding. We consider the origin of this difference.

First, we model the observed dielectric function from 0.05 to 3 eV. We can exclude phonon contributions that lie below 0.03 eV. We include a Drude-like term for free carriers plus a single Tauc–Lorentz oscillator, following Jellison. The contribution can be subtracted out within this model to simplify comparisons. The dielectric functions seen in Fig. 4 show a single peak due to bonding–antibonding transitions. We now analyse the optical dielectric constant \( \varepsilon_\infty \) that is, the low energy-limit of \( \varepsilon_1 \) in the range studied here, by the

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**Figure 1** Sample cross-section. a, Reference specimen. b, Sample investigated. 1: glass substrate, 2: Au layer, 3: semiconductor layer.

**Figure 2** Infrared reflectance spectra of an AgInTe film with a thickness of 0.65 \( \mu \)m. Blue: amorphous state, red: crystalline state. The solid lines describe the experimental data, whereas the dashed lines denote the simulation results.

**Figure 3** Infrared reflectance spectra of a Ge\(_{2}\)Sb\(_{2}\)Te\(_{5}\) film. Blue: amorphous state, red: crystalline state. The solid lines describe the experimental data, whereas the dashed lines denote the simulation results. On crystallization, the thickness decreased from 0.53 to 0.50 \( \mu \)m. The contributions of different phase-change film properties to the reflectance curve are marked.
Clausius–Mossotti model\textsuperscript{12}. If each atom of element \(i\) is assigned a polarizability of \(\alpha_i\), then

\[
\frac{\varepsilon_\infty - 1}{\varepsilon_\infty - 2} = \frac{\rho}{3\varepsilon_0 \sum_i n_i m_i \sum_j n_j \alpha_j},
\]

where \(\varepsilon_0\) is the permeability of free space, \(\rho\) is the density and \(m_i\) and \(n_i\) are the atomic weights and densities of element \(i\) respectively. A satisfactory fit is found for \(\alpha_{\text{Ge}} = 5.07 \times 10^{40} \text{C.m}^2\text{V}^{-1}\), \(\alpha_{\text{Sb}} = 7.82 \times 10^{40} \text{C.m}^2\text{V}^{-1}\) and \(\alpha_{\text{Te}} = 7.66 \times 10^{40} \text{C.m}^2\text{V}^{-1}\), describing all experimental values for \(\varepsilon_\infty\) within an average of 4%. This indicates that this model with constant polarizabilities will fit these and similar amorphous compounds.

We can also attempt to fit \(\varepsilon_\infty\) for the crystalline phases. We must first subtract out the low-energy Drude contribution from free carriers as shown in Fig. 4e,f. The resulting \(\varepsilon_\infty\) values are compared in Table 1. If both phases have the same atomic polarizabilities, then \(\varepsilon_\infty\) of the crystalline phase should only differ from the value of the amorphous phase owing to the density change. However, this is not the case; the experimental values are severely under-estimated, see Table 2.

We also analysed the \(\varepsilon_\infty\) values by a bond polarizability model, following the ideas of Philips and Levine\textsuperscript{13}. Assuming the

\[\text{Figure 4 Dielectric function } \varepsilon_1(\omega) \text{ and } \varepsilon_2(\omega) \text{ for various materials. a,b, Amorphous phase-change sample. c,d, Crystalline sample including Drude-type contribution. e,f, Crystalline sample with Drude contribution subtracted.}\]
Table 1 Optical dielectric constants and energy gaps. This table comprises the measured optical dielectric constants $\varepsilon_{\infty}$ of amorphous and crystalline phases of phase-change materials without Drude contribution, and Se, Te (refs 24,25). In addition, on the right-hand side the optical gaps $E_g$ are listed. The third column is a measure of resonance bonding in the crystalline state. AIST: Ag$_x$In$_{y}$Se$_{1-x-y}$Te$_y$.

<table>
<thead>
<tr>
<th>Material</th>
<th>Amorphous $\varepsilon_{\infty}$</th>
<th>Crystalline $\varepsilon_{\infty}$ % increase</th>
<th>Amorphous $E_g$</th>
<th>Crystalline $E_g$ % decrease</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge$_2$Sb$_2$Te$_4$</td>
<td>16.6 ± 0.3</td>
<td>36.2 ± 0.9</td>
<td>118</td>
<td>0.76</td>
</tr>
<tr>
<td>Ge$_2$Sb$_2$Te$_4$</td>
<td>14.8 ± 0.4</td>
<td>47.7 ± 0.8</td>
<td>222</td>
<td>0.77</td>
</tr>
<tr>
<td>GeTe</td>
<td>13.2 ± 0.2</td>
<td>33.2 ± 0.8</td>
<td>152</td>
<td>0.78</td>
</tr>
<tr>
<td>Ge$_2$Sb$_2$Te$_5$</td>
<td>16.0 ± 0.4</td>
<td>33.3 ± 0.8</td>
<td>108</td>
<td>0.77</td>
</tr>
<tr>
<td>Ge$_2$Sb$_2$Se$_5$</td>
<td>26.9 ± 0.7</td>
<td>0.41</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ge$_2$Sb$_2$Te$_6$</td>
<td>14.5 ± 0.3</td>
<td>29.8 ± 1.6</td>
<td>106</td>
<td>0.80</td>
</tr>
<tr>
<td>Ge$_2$Sb$_2$Te$_7$</td>
<td>15.6 ± 0.2</td>
<td>43.4 ± 1.2</td>
<td>178</td>
<td>0.79</td>
</tr>
<tr>
<td>AIST</td>
<td>19.6 ± 0.5</td>
<td>52.8 ± 1.5</td>
<td>169</td>
<td>0.63</td>
</tr>
<tr>
<td>Te</td>
<td>11</td>
<td>33.4</td>
<td>204</td>
<td>—</td>
</tr>
<tr>
<td>Se</td>
<td>5.7</td>
<td>9.79</td>
<td>72</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 2 Polarizability enhancement in the crystalline phase. Shown here are the calculated optical dielectric constants $\varepsilon_{\infty}$ of amorphous and crystalline phases using the Clausius–Mossotti relationship under the assumption of a constant polarizability for each element in all amorphous and crystalline phases, respectively. Whereas all amorphous materials can be described sufficiently well, no reasonable fit is possible for the crystalline phases. This implies that for the amorphous phases, the knowledge of the stoichiometry is sufficient to predict the optical dielectric constant $\varepsilon_{\infty}$, whereas this is not the case for the crystalline phases.

<table>
<thead>
<tr>
<th>Material</th>
<th>Amorphous Calculated</th>
<th>Error (%)</th>
<th>Crystalline Calculated</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge$_2$Sb$_2$Te$_4$</td>
<td>15.7</td>
<td>5.4</td>
<td>22.2</td>
<td>38.7</td>
</tr>
<tr>
<td>Ge$_2$Sb$_2$Te$_4$</td>
<td>15.7</td>
<td>6.1</td>
<td>36.4</td>
<td>22.7</td>
</tr>
<tr>
<td>GeTe</td>
<td>12.3</td>
<td>6.8</td>
<td>24.8</td>
<td>25.3</td>
</tr>
<tr>
<td>Ge$_2$Sb$_2$Te$_5$</td>
<td>15.7</td>
<td>1.9</td>
<td>24.9</td>
<td>25.2</td>
</tr>
<tr>
<td>Ge$_2$Sb$_2$Se$_5$</td>
<td>26.7</td>
<td>0.7</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ge$_2$Sb$_2$Te$_6$</td>
<td>13.8</td>
<td>4.8</td>
<td>23.7</td>
<td>20.5</td>
</tr>
<tr>
<td>Ge$_2$Sb$_2$Te$_7$</td>
<td>16.5</td>
<td>5.8</td>
<td>26.9</td>
<td>38.0</td>
</tr>
</tbody>
</table>

Figure 5 Schematic diagram demonstrating the origin of resonance bonding for Sb. On the left-hand side, one limiting case for bonding in an undistorted Sb phase is shown. A second limiting case is shown on the right-hand side. The solid can minimize its energy by forming a hybrid wavefunction, which is shown in the middle of this figure. This bonding is described as resonance bonding. The pronounced electron delocalization gives rise to an increased electronic polarizability.

atomic coordinations in the amorphous phases follow the $8$-$N$ rule, $Te = 2$, $Sb = 3$, $Ge = 4$, then $\varepsilon_{\infty}$ of the amorphous phases can be fitted by a sum of constant bond polarizabilities, whereas those of the crystalline phases cannot. This is demonstrated in the Supplementary Information.

We will identify the mechanism for this polarizability enhancement in terms of the difference in chemical bonding. As the bonding will have a profound impact on the local atomic arrangement, we will review briefly the structural motifs observed for crystalline and amorphous phase-change materials.

Early ideas of the local structure of amorphous semiconducting phases such as the continuous random network model suggested that the local coordination of the amorphous phase followed that of the parent crystalline phase. In phase-change materials, the bonding is different, but how? There have been a number of experiments to determine the local structure of the crystalline and amorphous states of phase-change materials. The amorphous phase was usually the focus of attention. In a first investigation, Taylor and co-workers used the covalent nature of bonding ($8$-$N$ rule, $N$ being the valence) to discuss the structural order in $Ge_xSe_xTe_{1-x}$ glasses with respect to the formation of homo- and hetero-polar bonds\cite{Kolobov2008}. Kolobov et al.\cite{Kolobov2008} showed by extended X-ray absorption fine-structure (EXAFS) spectroscopy that the local structure of the amorphous and crystalline phase of $Ge_xSb_yTe_z$, a prototype material, was considerably different, with the $Ge$ atoms being four-fold-coordinated in the amorphous phase, whereas the $Sb$ and $Te$ sites remain basically octahedral in both phases. Subsequently, Baker et al.\cite{Baker2008} gave evidence for $Ge$–$Ge$ bonds in the amorphous phase for this alloy. These authors stressed that the coordination numbers of the different elements in the amorphous phase are generally consistent with the $8$-$N$ rule of covalent bonding; $Ge = 4$, $Sb = 3$ and $Te = 2$. This finding has since been confirmed by a simultaneous analysis of X-ray and neutron diffraction data as well as EXAFS data\cite{Kolobov2008}.

In contrast, the coordination numbers of the crystalline phases are higher than expected from the $8$-$N$ rule, and are based on the distorted, six-fold-coordinated $A7$ rhombohedral structure of $GeTe$ (refs 18,19). The $A7$ structure is a distorted NaCl structure also adopted by $Sb$. Consider $Sb$ in the ideal NaCl structure. The $Sb$ atom has a filled valence $s$-orbital, and its bonding occurs between the $p$-orbitals which each contain one electron. To first approximation, these form three independent chains of $p$-states along the $x$, $y$ and $z$ directions. This leads to a half-filled band with a zero bandgap at the Fermi energy $E_F$. This structure is unstable with respect to a Peierls distortion, which forms alternative shorter and longer bonds along the chain, lowers the free energy and opens up a gap at $E_F$ (refs 20,21). Rhombohedral $GeTe$ is isoelectronic to $Sb$. It possesses the same structure, but exhibits a small amount of polar bonding, which opens up a small gap at $E_F$ even for the undistorted chain. The distortion increases the size of this gap. However, the size of the distortion is relatively small; thus, the change of the electronic system is rather small as well. Similar distortions were also found for ternary alloys such as $Ge_xSb_yTe_z$ (ref. 22).

The situation in which a single, half-filled $p$-band forms two bonds to the left and right (more than allowed by the $8$-$N$ rule) was called resonant bonding by Pauling\cite{Pauling1960}. This bonding is schematically shown in Fig. 5, which shows the (001) plane of a hypothetical simple cubic crystal of $Sb$. In this structure, each $Sb$ atom has six nearest neighbours, but only three $p$-electrons to facilitate covalent bonding between adjacent $Sb$ atoms. Different limiting cases can be identified as shown on the left- and right-hand side of Fig. 5. In reality, a superposition of these configurations is observed, which is schematically shown in the middle of this figure. This electron configuration has been coined as resonance bonding by Pauling. The pronounced electron delocalization, which characterizes resonant bonding, leads to a significantly increased electronic polarizability. This phenomenon is one of the fingerprints of resonance bonding.

The true crystal structure of $Sb$ is not a simple cubic structure, but the $A7$ structure, which can be described as a distorted simple...
cubic structure. This distortion increases electron localization because the two limiting electron configurations shown in Fig. 5 are no longer energetically equivalent. Thus, resonance bonding is weakened by the distortion, which is frequently denoted as a Peierls-like distortion. Hence, it is important to note that the distortion does not give rise to the large electronic polarizability and phase-change behaviour, but rather endangers it. The size of the contribution of resonance bonding can best be estimated from the relative increase of the electronic polarizability, \( \varepsilon_{\text{cryst}} / \varepsilon_{\text{amorph}} - 1 \). This number is listed in the third column of Table 1.

Resonance bonding is the cause of the large optical dielectric constant observed in many crystalline IV–VI compounds. It results in larger optical dielectric constants than in pair-bonded materials because it gives smaller average bandgaps (bonding–antibonding splitting) and larger optical matrix elements than electron pair bonding, as shown by Littlewood. The crystal structures of phase-change materials are all based on distorted cubic structures and all possess resonant bonding. It is therefore the cause of their higher optical dielectric constants. The existence of resonant bonding requires a longer-range order than the conventional electron pair bond of the 8–N rule. An electron pair only requires the ordering of the nearest neighbours forming the pair bond. Resonant bonding, on the contrary, requires the second and higher neighbours to be aligned. In the amorphous state, this higher level of ordering is not possible, and so the structure reverts to a simple 8–N rule structure, which requires a lower level of ordering, as noted by Lucovsky and White. This emphasizes that the bonding between the phases differs not only in coordination numbers as seen by EXAFS spectroscopy but also in their medium-range order.

The simplest example of resonant bonding is the trigonal structure of crystalline Se and Te. In these elements, the spiral chains of Se and Te are also distortions of simple cubic structures, in which there is a strong ordering between bonds on adjacent chains so that the p-orbitals again form into linear chains as in the A7 structure. However, on amorphizing the trigonal structure, this order is lost; their structure becomes more molecular with shorter interchain distances and longer interchain distances, and no obvious correlations between chains. The dielectric constant shows a strong fall from trigonal Te to amorphous Te and trigonal Se to amorphous Se (Table 1).

Thus, the decrease in \( \varepsilon_{\text{cryst}} \) values between the amorphous and crystal phases of phase-change materials can be taken as clear evidence that the medium-range order needed for resonant bonding is absent in their amorphous phases. This change in bonding between the amorphous and crystalline phases, with a strong rearrangement of the next-nearest neighbours, is at least as significant as the lowering of the Ge coordination to four or the formation of Ge–Ge bonds. This difference is more difficult to see in EXAFS.

The row-five elements Te and Sb have the strongest difference in bonding between the amorphous and crystalline phases, while still having a bandgap. Their crystalline phases have more resonant bonding, in that their short-bond and long-bond distances are closer than in the equivalent row-four elements Se and As. Thus, bonds in Se even in the crystalline phase are close to electron pair bonds (see data in Table 1). In this way, Se and selenides are good glass formers, whereas Te and tellurides are poor glass formers, and have the rapid crystallization rates needed for phase-change materials.

For all amorphous phases, we observe a very similar behaviour for both phase-change materials as well as sp\(^3\)-bonded, tetrahedrally coordinated covalent semiconductors. On the contrary, only phase-change materials exhibit a significant increase in polarizability on crystallization. This finding is attributed to a unique change of both structure and chemical bonding, giving rise to resonance bonding effects. Hence, from the viewpoint of property contrast, it is not the amorphous phase but the crystalline phase that is unique. The search for materials exhibiting the necessary optical contrast required for phase-change memory applications can hence be redirected. Those compounds need to be identified that are prone to the occurrence of this particular type of covalent bonding. As resonance bonding can only occur for semiconductors that possess unsaturated covalent bonds, all sp\(^3\)-bonded materials can immediately be excluded. In addition, materials that rearrange to form saturated covalent bonds by pronounced local distortions also will not possess resonance bonding.

Therefore, it becomes possible to derive structure–property maps based on an understanding for which compositions resonance bonding can be expected in the crystalline state. Such maps are not only useful because they identify candidates for storage applications. More importantly, the understanding of the bonding characteristics contained in such data will provide insight into systematic property changes, which can help to tailor materials for specific storage applications. The measurement scheme presented here provides both a recipe for the identification of candidates that show resonant bonding and quantifies the strength of this bonding mechanism. This information provides a basis for the discussion of differences in bonding as a function of stoichiometry.

**METHODS**

**SAMPLE PREPARATION**

To prepare the samples, a 150 nm Au layer is deposited using a homebuilt thermal evaporator (background pressure 2 × 10\(^{-5}\) mbar, 0.4 nm s\(^{-1}\) deposition rate, Au of 99.99% purity) onto a glass substrate. Subsequently, the phase-change films (500 or 1,000 nm) are deposited using an LS 320 von Ardenne system (background pressure 4 × 10\(^{-7}\) mbar, 20 s.c.c.m. Ar flow, deposition rates 0.1–0.2 nm s\(^{-1}\), operating in constant power mode using 20–25 W) using stoichiometric targets of 99.99% purity. The as-deposited amorphous films were annealed in Ar atmosphere for 30 min at temperatures about 20 °C above the corresponding crystallization temperature to obtain polycrystalline samples. The structure of the phase-change samples was checked by X-ray diffraction. The film densities were determined by accompanying measurements on 80 nm thin films with X-ray reflectometry. The phase-change layer thickness was determined from reference samples prepared in the same sputter session using an Alpha-Step 200 profilometer (Tencor Instruments). Nine thickness values were taken at different positions and their average value was used as a reference for the optical simulations.

**OPTICAL MEASUREMENTS**

Reflectance spectra have been measured in the range from 0.025 to 1 eV, using a Bruker IFS 66v/s spectrometer with a resolution of 0.12 meV using a globar. The reflectance spectra of the reference and the sample were measured subsequently to exclude drift effects. For normalization, the final spectrum was obtained by dividing the measured spectrum by the reference spectrum. The angle of incidence of the incoming beam was kept constant at 10° with respect to the surface normal. The relative measurement error for the reflectance is 0.2% in the measured wavelength range.

Ellipsometry spectra have been measured in the range from 0.7 to 5.2 eV using a Woollam M-2000UI using angles of incidence of 60°, 65° and 78°. Deuterium and halogen lamps served as light sources. As detectors, a silicon charge-coupled device camera was used for the visible and ultraviolet range, whereas the lower energy range was covered by an InGaAs diode array. This detector uses 884 channels with an average resolution of about 7 meV. Both ellipsometry and FTIR spectra have been recorded at room temperature.

**MODELLING OF THE SPECTRA**

Both experimental ellipsometry and FTIR spectra were analysed simultaneously in the range from 0.05 to 3 eV using the SCOUT software. The model dielectric function \( \varepsilon(\omega) \) used is composed of the following summands: (1) a constant,
which accounts for the polarizability in the higher energy range (for example, contribution of core electrons), (2) a Drude-type contribution for free carriers in the case of the crystalline samples, and finally, (3) a Tauc–Lorentz oscillator\(^{13,33}\) to describe the onset of optical transitions:

\[
E(\omega) = E_{\text{const}} + E_{\text{Drude}}(\omega) + E_{\text{Tauc-Lorentz}}(\omega)
\]

\[
E_{\text{Drude}}(\omega) = \frac{\omega_p^2}{\omega(\omega + i\gamma)}
\]

\[
\text{Im}(E_{\text{Tauc-Lorentz}}(\omega)) = \frac{1}{\omega} \frac{S^2(\omega - \omega_g\epsilon)}{\omega^2 + \frac{\omega^2}{\omega_g^2}} \Theta(\omega - \omega_g\epsilon).
\]

A layer stack as presented in Fig. 1b was simulated, with the dielectric function of gold taken from a database. The latter was checked to be in excellent agreement with the optical properties of the reference specimen, the gold oscillator. The optical gap \(E_g\) was identified as the energy where the absorption or exceeds 10,000 cm\(^{-1}\). The optical dielectric constant \(\varepsilon_{\infty}\) was determined from the dielectric function as \(\varepsilon(0.05\text{eV}) = \varepsilon_{\infty}\) in the crystalline case after subtracting the Drude contribution.

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Author information

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Correspondence and requests for materials should be addressed to M.W.