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Phonon scattering at a crystal surface from *in situ*–deposited thin films

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We have studied diffuse scattering of phonons from *in situ*–deposited thin films (average thicknesses from 1 Å to 1 μm) using boundary-limited thermal conductivity measurements of the Si substrate. Our temperature range is 0.05–2 K corresponding to dominant phonon frequencies from 5 to 180 GHz. We show that the scattering occurs within the films themselves, not at the sample-film interface, and give evidence that this scattering is caused by structural irregularities of the thin films. Our findings have a direct bearing on the Kapitza resistance problem.

Thin films or interface layers play a fundamental, yet poorly understood, role in phonon-scattering processes at a surface.[1,2] There has been much speculation as to the types of phonon interactions that may be occurring. Interface states such as resonant scatterers[3] and two-level tunneling systems[4] have been proposed, and the effects of surface roughness have been considered,[5] but data on well-characterized surfaces are as yet insufficient to either confirm or refute these models. In this paper we elucidate this situation through a systematic study of phonon scattering at a crystal surface by deposited thin films. The species, thickness, and structure of the films are reproducibly controlled and varied *in situ* at low temperature. We have probed the transition from specular to diffuse scattering with increasing temperature (increasing phonon frequency) as a function of these film properties, and conclude that the scattering occurs within the films themselves and not at the interface. We have identified the source of the scattering and suggest that accidental impurity films with small islandlike structure will scatter high-frequency phonons via a similar process, and may be responsible for strong phonon interactions at surfaces, such as in the anomalous Kapitza conductance.[1]

Thermal conductivity measurements in the boundary scattering regime can be used to study phonon scattering at a crystal surface.[2] A roughened crystal surface leads to completely diffuse scattering and limits the phonon mean free path to the sample width, while clean, polished surfaces reflect phonons specularly, resulting in a larger effective mean free path.[6] Previously,[2] films were deposited outside the cryostat and therefore spurious effects due to exposure to air between depositions could not be ruled out. Here, thin films of Ne, H_2, and D_2 are produced and removed *in situ* without warming above a few degrees Kelvin, thus avoiding this potential source of contamination. In this way we are able to introduce defects onto the surface in a controlled, reproducible way.

Our sample is a Si crystal of square cross section ($5\times5\times50$ mm^3) which is Syton polished on its four long faces, cleaned in a hot 5:1:1 solution of H_2O:H_2O_2:NH_4OH and mounted on the mixing chamber of a dilution refrigerator (Fig. 1). Next to the sample is a small torsional oscillator etched from a silicon wafer, similar to the design developed by Kleiman *et al.*[7] A cylindrical porous Vycor tube surrounds both the sample and oscillator and acts as our gas reservoir. During the cooldown, it adsorbs either Ne, H_2, or D_2 into its pores. At low temperature the Vycor tube is heated slowly until the adsorbed gas desorbs from all sides and condenses onto the sample and oscillator. Film thickness is measured by monitoring the change in resonant frequency of the oscillator. The oscillator has a quality factor of $\sim10^7$ at 3 K and a stability of better than $1{:}10^9$ over several hours, whereas a shift of $1{:}10^7$ corresponds to a monolayer of Ne. The range from 1 Å to 1 μm average film thickness is, therefore, easily covered. In addition, the residual pressure in the cryostat can be determined by observing the time it takes for one monolayer of residual gas to plate out onto the oscillator. Since we observe a frequency drift of only $\Delta f/f \leq 10^{-8}$ over three days when the cryostat is cold, we can determine that the residual pressure is $<5\times10^{-12}$ torr. All our depositions and measurements are therefore done under truly clean (ultrahigh-vacuum) conditions.

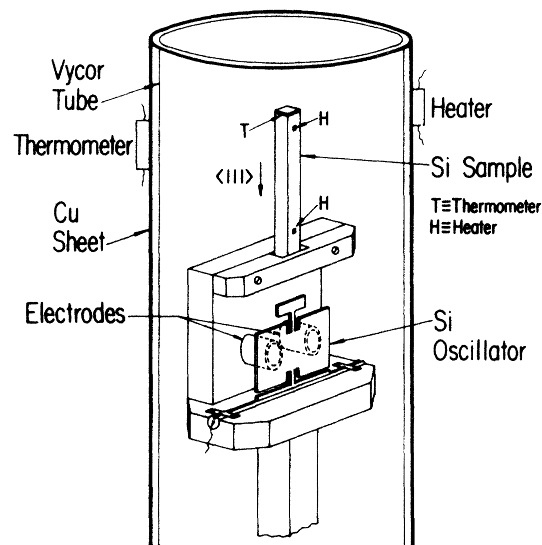

FIG. 1. Experimental setup. Gas is adsorbed into the pores of the Vycor tube during the cooldown. A deposition is made at low temperatures by heating the tube. The film thickness is monitored by the Si torsional oscillator. A two-heater method is used to measure the thermal conductivity.

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The data are presented as the reciprocal of the phonon mean free path $l^{-1}(T)$, which is proportional to the diffuse scattering rate. We determine l^{-1} from the thermal conductivity $\Lambda = \frac{1}{3}Cvl$, where C is the specific heat and v is an average speed of sound. Figure 2 shows $l^{-1}(T)$ due to films of Ne, H_2, and D_2 as well as a clean and a rough (sand-blasted) surface.

The clean surface is found to be highly specular[6] (and reproducibly so) to thermal phonons at these temperatures (<1 K, i.e., $\lesssim 90$ GHz). At higher phonon frequencies, however, the residual "dirt" that is present on all real surfaces is known to scatter the phonons[1] and extraordinary surface treatments, such as *in situ* cleaving or laser annealing, are necessary in order to produce a good surface. Thus, the advantage of working at lower phonon frequencies is that such difficult techniques are unnecessary. So even though the physical perfection of our clean surface is not known, it is a good substrate—at these phonon frequencies—on which to study the effects of adsorbed films.

The next point we wish to make is that our data imply that the phonons are scattered within the film, and not at the interface. Several different coverages of H_2 are also shown in Fig. 2. The fact that it takes a relatively thick coverage (150 Å) of H_2 to cause any diffuse scattering, and that this scattering increases with film thickness, is the first indication that the diffuse scattering is associated with processes in the thin film itself and not with states localized at the sample-film interface. As film thickness is increased, a maximum scattering rate is reached, whereupon the addition of further H_2 (up to 1 μm) does not increase the scattering rate any further. This "thick"-layer scattering limit also exists for Ne and D_2 and is shown in Fig. 2 as well. This means that no matter how thick a film is deposited onto the crystal surface, a certain fraction of the phonons continues to be specularly reflected. In the absence of diffuse scattering at the interface itself, this fraction should be equal to the fraction of specularly reflected phonons one would calculate on the basis of acoustic mismatch between Si and these films. We have performed this calculation,[6] taking into account our sample geometry, and the results for Ne, D_2, and H_2 are indicated by the arrows in Fig. 2, showing good agreement with our thick-layer limits. Thus, we conclude that the diffuse scattering occurs in the thin films themselves, while the scattering at the interface is specular.

Our measurements also help us to understand the role of film structure in diffuse scattering processes. For Ne, changing the coverage yields results that are characteristically different from H_2. The data for Ne (Fig. 3) are characterized by a threshold temperature below which l^{-1} is equal to the l^{-1} of the clean specular limit, and above which diffuse scattering occurs. As temperature is further increased, l^{-1} eventually merges with the thick-layer limit for Ne. This threshold temperature decreases monotonically with increasing coverage. In these experiments the Ne is deposited when the sample is held at 1 K. Figure 4 compares the scattering data for two Ne films of the same

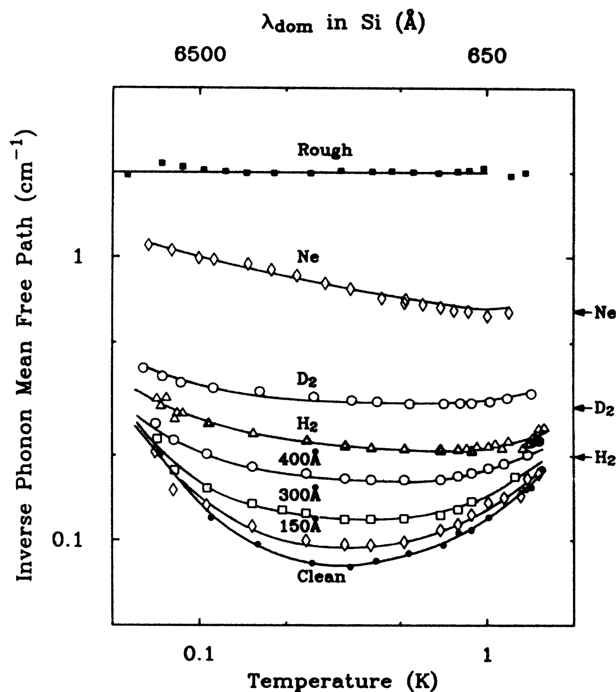

FIG. 2. Thick-layer scattering limits for thin films of Ne, H_2, and D_2, and coverage dependence of H_2. The arrows on the right show the calculated acoustic mismatch between Si and Ne, D_2, and H_2 for our sample geometry. The rise in the data at the lowest temperatures is not an actual increase in diffuse scattering. It is due to an angular- and frequency-dependent boundary resistance at the sample base.

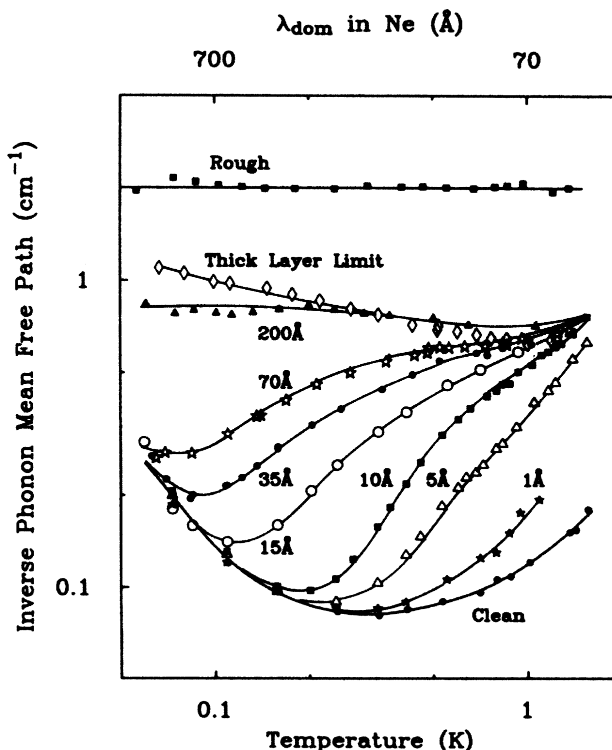

FIG. 3. Diffuse scattering rates for different coverages of Ne on Si. The sharp threshold behavior is due to the island structure of the Ne film.

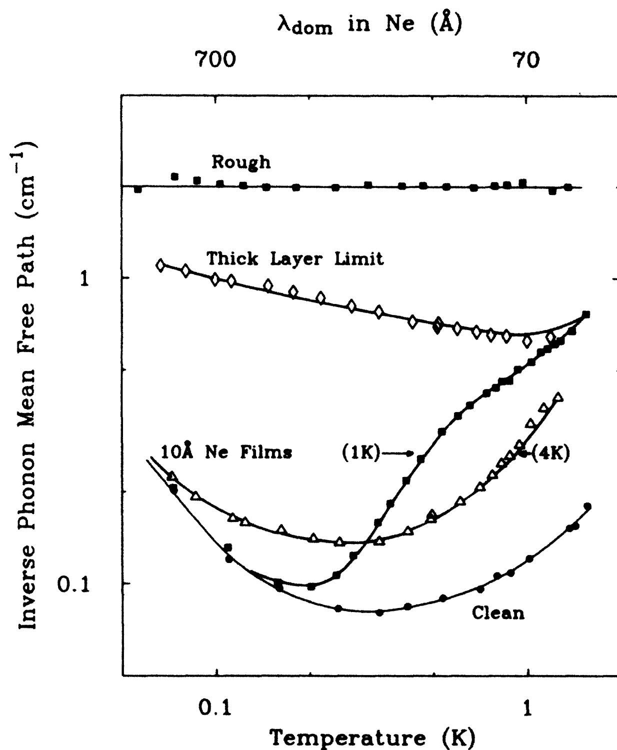

FIG. 4. Diffuse scattering rate for two Ne films of the same average thickness (10 Å), deposited at 1 and 4 K, respectively. Films deposited at 1 K show a threshold temperature indicating an island structure, while films deposited at 4 K have a smoother profile, indicating they are continuous.

average coverage (10 Å); one deposited onto the sample when it was at 1 K, the other deposited when it was at 4 K (above 4 K the condensed gas desorbs from the sample). The data for the 4-K-deposited film do not show a sharp threshold temperature and resemble the profiles of the H_2 films. At the lowest temperature there is more diffuse scattering, and at the higher temperatures there is less scattering than in its 1-K counterpart. The difference in the scattering profiles, therefore, is not due to the phonons interacting with Ne differently than with H_2, but rather to differences in how the films are deposited. The substrate temperature during a deposition can significantly affect the structure of a thin film. In particular, films can be made continuous or discontinuous. Now consider the effect of this difference in structure on diffuse scattering. First, it is clear that bulk scattering is negligible, especially in the very thin films, as phonon mean free paths in even fully amorphous materials are between 10^4 and 10^5 Å at these temperatures. However, structural irregularities in the thin films could be effective in scattering the phonons. We make the analogy to scattering from surface irregularities,[8] keeping in mind that all the scattering is mediated by acoustic mismatch between the Si sample and the thin film. If a film is discontinuous or has an island structure, one would expect geometrical scattering (which is temperature independent) when $\lambda \ll d$, where λ is the phonon wavelength and d is the island size. When $\lambda \gg d$, scattering should die away quickly (ideally as λ^{-4}, the analogue of Rayleigh scattering at a surface). For $\lambda \sim d$ one expects a crossover, which would correspond to the transition between specular and diffuse scattering that we see in the Ne data of Fig. 3 (one might also expect a resonance when $\lambda \simeq d$, but this would be difficult to see with a thermal conductivity measurement and a distribution of island sizes). For continuous films, structural variations may be smoother and occur on a scale which is larger than the phonon wavelengths at even our lowest temperatures. In this limit, we are always in the geometrical scattering regime, and therefore the scattering will be temperature independent. The amount of specularity will depend on the details of the structural irregularity. This temperature-independent scattering can be seen in the H_2-film data in Fig. 2. The 4-K Ne film in Fig. 4 is clearly somewhere in between these two limits, i.e., not islandlike but not as smooth as the H_2 films. Our interpretation, that the observed differences in the diffuse scattering profiles are due to variations in structural irregularities, is supported by data obtained on films deposited outside the cryostat in an evaporator.[2] Scattering data on thin Au films showed sharp threshold temperatures similar to the Ne films in Fig. 3. Electron micrographs showed that these Au films were discontinuous with an islandlike structure, and the dominant phonon wavelength, λ_{dom}, in Au at the threshold temperature was indeed found to be comparable to the island size. By contrast, deposited a-Si films, which appeared smoother, resulted in a $l^{-1}(T)$ very much like that of the 4-K Ne film of Fig. 4. The picture of the role of structural irregularities proposed here describes, at least qualitatively, the main features of our data. However, there are details that remain unclear, including why condensed gas films appear smoother (i.e., have no sharp threshold temperature) when they are deposited at a higher temperature. Phonon trapping in the thin films must also play an important role, as may scattering from internal boundaries or elastic inhomogeneities.

As we stated earlier, residual surface impurities are known to scatter high-frequency phonons diffusely and lead to an anomalous Kapitza conductance.[1] An outstanding question is how the phonons interact with these presumably very thin films. The work we have reported on here shows that even very thin films (for Ne, an average thickness of 1 Å or 0.5 of an atomic layer averaged over the entire surface) scatter the phonons from their structural irregularities. At higher phonon frequencies (shorter wavelengths) one would expect that even thinner discontinuous films (smaller islands) would scatter phonons by this same mechanism. Shiren[5] has shown that scattering from surface irregularities can indeed explain certain anomalous Kapitza resistance measurements when the generation and scattering of surface waves is taken into account. Although he was considering surface roughness, the theory is also applicable to irregularities caused by surface adsorbates if the mass density of the adsorbate is factored in appropriately. Finally, we note that even for our "clean," polished surface, there is an upturn of l^{-1} as T increases above 0.5 K (Figs. 2–4). We believe that this is due to diffuse scattering by the residual surface impurities or irregularities. This agrees well with previous studies of the temperature (or frequency) dependence of phonon re-

flection and transmission at an interface between Si and either ^{4}He,[9,10] H_2,[11] or N_2,[9] which also showed that all anomalous transmission dies out below ~ 1 K or 80 GHz. Thus, scattering from structural irregularities in discontinuous adsorbed impurity layers offers a natural explanation for anomalous Kapitza conductances.

To conclude, we have shown that phonons are scattered by both continuous and discontinuous thin films. Diffuse scattering occurs in the films themselves; diffuse scattering by some kind of unknown interface states is negligible. Film structure is very important in determining the amount of diffuse scattering, and it appears that scattering by structural irregularities may be the dominant process involved. In particular, island structures lead to a sharp threshold temperature in the diffuse scattering profile. The impurity layers present on all conventional "clean" surfaces may cause this type of scattering as well, offering a simple explanation for the strong phonon coupling seen in many earlier experiments carried out at frequencies corresponding to $T \geq 1$ K, including Kapitza resistance studies.

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