Two-level systems in evaporated amorphous silicon

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ABSTRACT

In *e*-beam evaporated amorphous silicon (*a*-Si), the densities of two-level systems (TLS), n_0 and $\overline{P}$, determined from specific heat C and internal friction Q^{-1} measurements, respectively, have been shown to vary by over three orders of magnitude. Here we show that n_0 and $\overline{P}$ are proportional to each other with a constant of proportionality that is consistent with the measurement time dependence proposed by Black and Halperin and does not require the introduction of additional anomalous TLS. However, n_0 and $\overline{P}$ depend strongly on the atomic density of the film (n_{Si}) which depends on both film thickness and growth temperature suggesting that the *a*-Si structure is heterogeneous with nanovoids or other lower density regions forming in a dense amorphous network. A review of literature data shows that this atomic density dependence is not unique to *a*-Si. These findings suggest that TLS are not intrinsic to an amorphous network but require a heterogeneous structure to form.

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1. Introduction

At low temperatures, the thermal, acoustic, and dielectric properties of amorphous materials are dominated by low energy excitations that are not normally found in crystalline materials [1]. It was originally believed that these excitations were intrinsic to the amorphous state since they occurred with roughly the same density in all amorphous solids and were independent of the chemical constituents of the materials [2,3]. However, recent measurements have shown that TLS can be suppressed in certain thin film materials suggesting that the vapor deposition process leads to a fundamentally different energy landscape than quenching from a liquid [4–10]. The two-level systems (TLS) model successfully describes many low temperature phenomena, such as the linear temperature dependence of the specific heat and the internal friction plateau. The TLS model is an incomplete description of the amorphous state though as it does not describe other ubiquitous low temperature phenomena, such as the excess T^3 specific heat or the thermal conductivity plateau [1,11,12].

Systematically testing the TLS model in amorphous solids has proven difficult as the physical origin of the TLS in these materials is unknown. Understanding the origin of these excitations and how to controllably remove them has gained new urgency as decoherence caused by TLS is a major roadblock for quantum devices [13,14]. Recently we have shown that the TLS in *a*-Si can be removed by increasing the atomic density of the film, which depends on both the film thickness *t*

and growth temperature T_S, and that the TLS are linked to the excess T^3 heat capacity [8,9]. In this article, we use the tunability of the TLS in *a*-Si to show that the TLS are described by the standard TLS model and that anomalous TLS, those that contribute to C and not Q^{-1}, are not required to explain our results.

The TLS model assumes that neighboring minima in the potential energy landscape of an amorphous solid can be treated as double-well potentials where the wave function overlap between wells creates a finite tunneling probability which splits the ground state energy creating the TLS [11,12]. The TLS must be broadly distributed in the energy landscape to describe the experimental results. Physically, the TLS are thought to correspond to single atoms or groups of atoms with energetically similar configurations that are separated by energy barriers on the order of 100 K with tunnel splittings <1 K [15]. It has been suggested that the amorphous structure must be open and have low coordination for the TLS to form [11]. Structural rigidity is known to play a key role in the glass forming ability and elastic properties of amorphous solids [16] and the rigid four fold coordination in tetrahedrally bonded materials, such as *a*-Si and *a*-Ge, is generally thought to prevent the formation of TLS [11]. There are conflicting results in the literature on whether TLS occur in *a*-Si and *a*-Ge and it has been debated whether the TLS in these systems are the same as those found in other glasses, such as *a*-SiO$_2$ [17–23]. The TLS density in tetrahedrally bonded materials depends strongly on the preparation technique suggesting that the TLS are due to some microstructural detail of the material [5,24]. For example, it was previously thought that hydrogen played a key role in removing TLS from *a*-Si [4] but our recent results show that the reduction in TLS in the hydrogenated material was likely the result of increasing T_S [9].

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The presence of low energy excitations can be seen experimentally in the low temperature specific heat C which, for an amorphous dielectric, has the form [2],

$$C = c_1 T + c_3 T^3 \tag{1}$$

where c_1 is the linear specific heat due to the low energy excitations. In the TLS model, c_1 for a-Si, in units of J mol^{-1} K^{-2}, is expressed as

$$c_1 = \frac{\pi^2}{6} k_B^2 n_0 \frac{N_A}{n_{Si}}, \tag{2}$$

where k_B is Boltzmann's constant, n_0 is the density of TLS, N_A is Avogadro's number, and n_{Si} is the Si number density. [25] $n_0 \approx 10^{45}$ J^{-1} m^{-3} for most glasses [2].

$$c_3 = c_D + c_{ex} \tag{3}$$

is larger than the specific heat due to phonons c_D. $c_{ex} \approx c_D$ and is thought to be caused by excess, non-propagating vibrational modes.

At low T, the interaction between the TLS and elastic/thermal waves leads to loss in acoustic measurements [26] and the T^2 temperature dependence of the thermal conductivity [1,2]. The interaction between acoustic waves and TLS leads to dissipation, or internal friction Q^{-1}, and is observed as a temperature independent plateau in at $T \approx 0.1$–10 K in Q^{-1}. In the TLS model, the plateau Q_0^{-1} is expressed as

$$Q_0^{-1} = \frac{\pi}{2} \frac{\overline{P} \gamma_i^2}{\rho v_i^2}, \tag{4}$$

where i indicates the polarization of the wave (longitudinal or transverse), $\overline{P}$ is the spectral density of TLS, $\gamma_i \sim 0.1 - 1$ eV is the coupling energy between TLS and acoustic waves [27], ρ is the mass density, and v_i is the sound velocity. $Q_0^{-1} \approx 10^{-4}$ ($\overline{P} \approx 10^{44}$ J^{-1} m^{-3}) and varies little for bulk quenched glasses of differing chemical composition for both wave polarizations [3]. The TLS density measured by Q^{-1}, acoustic attenuation, or thermal conductivity is often described as "universal" due to the insensitivity of the measurement results to chemical composition and excitation frequency [3] and is often regarded as a measure of the intrinsic TLS described by the TLS model [27].

Comparison of the TLS densities measured by C and Q^{-1} show that $n_0 \approx 20 \overline{P}$ for the materials where both have been measured [1,2, 27–31]. Measurements such as Q^{-1} are performed in the frequency domain with an excitation frequency ω. These measurements yield the spectral TLS density as only those TLS with relaxation time τ, satisfying $\omega\tau \sim 1$, are probed. Specific heat measurements on the other hand measure all TLS that can equilibrate with the phonon bath on the time scale of the measurement. Black and Halperin considered how a distribution of relaxation times in the TLS model would affect C measurements [32, 33] and found that

$$n_0 = \frac{1}{2} \overline{P} \ln\left(\frac{4\tau}{\tau_{\min}}\right), \tag{5}$$

where τ is the measurement time and $\tau_{\min}$ is the minimum TLS relaxation time which is estimated to be $\approx 10^{-9}$ s from comparison of n_0 and $\overline{P}$ for a-SiO$_2$ [32]. It is assumed that $\tau_{\min}$ varies little between amorphous materials. The predicted logarithmic time dependence was found in C measurements where $\tau < 100$ μs [30]. However for longer τ, C increased faster than predicted by Eq. (5) which suggested either a non-uniform spectral distribution of TLS [30] or that additional anomalous TLS contribute to C at longer τ [30,33].

In this paper, we compare the TLS densities n_0 and $\overline{P}$ from C and Q^{-1} measurements, respectively, of e-beam evaporated a-Si films and show that the low energy excitations are described well by the TLS model over three orders of magnitude in TLS density. Both C and Q^{-1} at low T are

typical of amorphous materials containing TLS: C is linear in temperature and Q^{-1} has a temperature independent plateau. Both measures of the TLS density are found to depend strongly on the atomic density of the film n_{Si} which varies with deposition temperature T_S and film thickness. The highest density films have TLS densities near or below the detection level of either technique, while lower density films have a significant TLS density that is similar to other amorphous solids. The agreement between n_0 and $\overline{P}$ shows that additional, anomalous TLS are not required explaining our results. We suggest that a-Si has a heterogeneous structure consisting of voids, or some other low density structure, surrounded by a dense backbone network. Finally, we compare our a-Si results to literature data on other materials where the TLS density was found to vary and atomic density was available. We observe a qualitatively similar density dependence in these systems which suggests that TLS in the low coordination bulk glasses are not an intrinsic result of disorder but also depend on the nano-scale structure of the materials.

2. Experimental procedure

A-Si thin films were prepared by e-beam evaporation at a base pressure of $\sim 1 \times 10^{-8}$ Torr and a growth rate of 0.05–0.1 nm/s. Growth temperature T_S was varied from 45°–400 °C. Films were grown separately on membrane-based nanocalorimeters and single crystal double paddle oscillators (DPO). The film thickness t was varied for the C measurements while the Q^{-1} films were all nominally 300 nm thick to ensure an adequate measurement signal. Thicknesses were measured on films grown on neighboring substrates using a KLA-Tencor Alpha-Step IQ profilometer with an error of 1%–4% depending on the film thickness. The uncertainty in t is the dominant source of error except in some samples where C below 10 K was less than 10% of the total measured heat capacity; in that case random error in the measurement dominates. The average film densities were determined from Rutherford backscattering (RBS). All of the films were found to have a thin surface oxide (1–2 nm). The lower density films grown at 45 °C films had $\approx$4–5 at.% oxygen below the surface while the higher T_S films had $\leq$1 at.% oxygen with concentration profiles consistent with post-deposition diffusion into the film.

Transmission electron micrographs (TEMs) were taken in cross sections on films grown at 45 °C and 400 °C and are shown in Fig. 1. The low magnification TEM shows a columnar growth structure, which is commonly seen in evaporated films, with the TS = 400 °C film having larger diameter columns (8 ± 5 nm) than the 45 °C film (4 ± 3 nm). The column diameters appear constant throughout the thickness of the films. The high resolution TEM shows that the films are fully amorphous with no lattice fringes or diffraction peaks. Similarly, X-ray diffraction showed no peaks. Dangling bond densities n_{ESR} were determined from electron spin resonance (ESR) measurements where the gyromagnetic ratio g = 2.0055 as is typical for isolated, neutral dangling bonds in a-Si [34]. Raman scattering measurements were performed using the 514.5 nm line of an Ar ion laser [8].

Heat capacity measurements were made from 2–300 K using a microfabricated nanocalorimeter. Details of the measurement technique are provided elsewhere [35–37]. For these measurements a 20 nm a-AlO$_x$ diffusion barrier was sputtered onto the a-Si sample before deposition of the Cu film which is used to ensure the sample is isothermal during the measurement. The calorimeter with only the a-AlO$_x$ and Cu films was measured separately for subtraction of the background heat capacity.

Q^{-1} measurements were made from 0.3–300 K using the antisymmetric torsional mode of the DPO at 5500 Hz [38]. The shift in the resonant frequency of DPO after the deposition of the film gives the shear modulus $G = \rho v_t^2$ where v_t is the transverse sound velocity. The longitudinal sound velocity v_l was measured using an ultrasonic pump/probe technique [39].