Evidence for a large phononic band gap leading to slow hot carrier thermalisation

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Abstract. It has been proposed that the rate of hot carrier thermalisation can be slowed down if there is a sufficiently large gap in the phonon dispersion for a bulk material. This phenomenon is critical for the development of high efficiency hot carrier solar cells to minimise energy loss to thermalisation. A gap where the minimum of the optical branches is at least twice that of the maximum of the acoustic branches can prevent the primary pathway where optical phonons loses energy, the Klemens’ decay mechanism. The large gap in the phonon dispersion eliminates the Klemens’ decay pathway due to energy and momentum conservation laws. This enables the electron population to remain hot by allowing sufficient time for optical phonons to re-scatter its energy to electrons. Binary compounds with a large mass difference between the two constituent atoms and high level of crystal symmetry such as zirconium nitride and hafnium nitride (HfN) have such a gap in their phonon dispersion. HfN thin films have been sputtered on silicon and quartz substrates. Characterisation of hot electron lifetimes in HfN films have been performed using ultrafast transient absorption spectroscopy. Preliminary analysis of transient absorption data, both spectra and time evolution has indicated high carrier temperatures with a nanosecond long decay time. It is postulated the long hot carrier lifetime is due to the large phononic gap.

1. Introduction
Thermalisation occurs when hot carriers relax to the conduction band edge from elevated energy levels above the conduction band. Hot carriers refer to electrons or holes with energies above the conduction band edge or below the valance band edge. The distribution of these energetic carriers can be described by the Fermi-Dirac distribution at a higher temperature, hence the name hot carriers. Thermalisation of hot carriers in photovoltaic devices makes up a significant portion of energy lost as heat which cannot be converted to electricity. The optimal semiconductor bandgap for a solar cell to achieve maximum energy conversion efficiency is characterised by a trade-off between energy lost to the lattice via hot carrier thermalisation and photons not absorbed below the bandgap [1]. At the optimal band gap of 1.3 eV as described by the Shockley-Queisser limiting efficiency of p-n junction solar cells, the energy lost due to thermalisation is 30% and below E_g loss is 25% of the incident illumination [2]. The Hot Carrier solar cell aims to address these two fundamental loss mechanisms that limit the efficiency of conventional p-n junction solar cells [3, 4, 5].
The Hot Carrier solar cell aims to capture the hot carrier population of photo-generated electron-hole pairs before thermalisation processes occur. This enables a low band gap material to be used as a photon absorber thus minimising energy loss due to both thermalisation and sub bandgap photons not absorbed. The hot carriers are separated and extracted to the external circuit by the use of energy selective contacts, where only carriers of an elevated energy are collected. The absorber is required to maintain a hot carrier population for a long enough time for the hot carriers to be extracted. A long hot carrier lifetime can be achieved by exploiting or engineering the phononic properties of materials.

We investigate carrier dynamics and phonon properties hafnium nitride (HfN) in the context of an absorber layer for the Hot Carrier solar cell. Materials that exhibit long hot carrier lifetimes can be used in technologies such as thermoelectric, plasmonic and thermionic emission devices.

2. Thermalisation of hot carriers and slowed carrier cooling

In a semiconductor, electrons are able to be excited into the conduction band from the valence band from absorbing the energy of the incident photon if the photon has more energy than that of the semiconductor’s bandgap. Elastic carrier-carrier scattering occurs within several femtoseconds, which redistribute the energy of the hot carrier population to a Fermi-Dirac distribution described by a temperature elevated above the lattice temperature. The hot carrier population subsequently thermalises to the band edge which occurs within 10 - 100 ps. The mechanism for thermalisation involves interactions between electrons and optical phonons as described by Fröhlich interactions [6]. Energetic carriers emit optical phonons which decay into acoustic phonons. This is the point where the energy is lost and irretrievable because acoustic phonons have a large group velocity and are able to cross interfaces easily.

Decay of high energy optical phonons to lower energy acoustic phonons is dominated by processes known as Klemens decay and Ridley decay. These decay mechanisms adhere to conservation of energy and momentum laws. Klemens decay occurs when a phonon in the optical branch decays into two acoustic phonons with half the energy but opposite and equal momentum [7]. Ridley decay occurs when an optical phonon decays to an optical phonon of lower energy and an acoustic phonon [8].

It is proposed that by preventing the decay of optical phonons to acoustic phonons can slow the carrier cooling rate [9]. If there exist no pathway for optical phonons to decay into acoustic phonons a hot optical phonon population can be maintained. Electrons can reabsorb optical phonons hence maintaining a hot carrier population. A gap between the optical and acoustic branches of the phonon dispersion such that the minimum of the optical branch is at least twice that of the maximum of the acoustic branch can remove the dominate decay pathway, Klemens decay. Hafnium nitride has a wide phonon gap because of the difference in mass between the constituent atoms and the highly symmetric rock-salt crystal structure [10]. Figure 1 shows the large gap in the calculated phonon dispersion of hafnium nitride.

![Figure 1. Phonon dispersion (left) and phonon density of states (right) of HfN [10].](image)
3. Hafnium nitride deposition
Thin films of HfN were deposited on Si(100) and quartz substrates using an AJA ATC-2200 magnetron sputtering system by DC sputtering of a 4 inch Hf target of 99.9% purity in a mixed argon and nitrogen atmosphere. An argon gas flow rate of 15 sccm mixed with nitrogen gas flow of 1.5 sccm was used. Before deposition the deposition chamber was pumped down to a base pressure of lower than $2.5 \times 10^{-6}$ Torr. The samples were deposited with constant DC power of 50 W and at a pressure of 1.5 mTorr. Deposition occurred with the substrates heated to approximately 450 °C. The films were deposited for 1 hour. The Si(100) substrates were chemically cleaned using RCA1, RCA2 solutions and HF dip prior to loading into the load lock chamber. Prior to the film deposition, the substrates were thermally degassed at 550 °C for 1 hr and the sputter target was sputter-cleaned for, at least 10 minutes, to remove surface oxides and other impurities.

The deposited HfN films were around 45 nm as measured using a surface profilometer. From x-ray diffraction measurements, the HfN films are polycrystalline with a preferred HfN(100) orientation on Si(100) substrates and no preferential orientation on quartz substrates. From Raman spectroscopy results, as shown in figure 2, shows close agreement between the Raman spectrum and the calculated phonon dispersion of the HfN films. The broad Raman peak around 500 cm$^{-1}$ is associated with zone centred optical mode and Raman peak at 140 cm$^{-1}$ is associated with the acoustic peak. Although observations of acoustic peaks are not expected via Raman spectroscopy the acoustic peak may be attributed to the non-stoichiometric HfN films leading to point defects breaking the crystal symmetry or phonon mode folding of the acoustic branches at grain boundaries of the polycrystalline film.

![Figure 2. Measured Raman spectra of deposited HfN film.](image)

4. Ultrafast transient absorption spectroscopy
The fs pump-probe experiments were performed with a transient absorption (TA) spectrometer (FemtoFrame II, IB Photonics). The excitation source is a 400 nm pulse by an OPA laser (TOPAS, Spectra Physics) with 100 fs duration and 1 kHz repetition rate. The probe beam of white light continuum was generated by focusing the 1 kHz Ti:Sapphire amplified laser (Spitfire, Spectra Physics) into BBO crystal, and detected by a polychromator-CCD.

Figure 3 is the TA spectrum at various time delays. Immediately after the ultra-short laser irradiation, electrons are excited to the high excited state. Ultrafast e-e scattering occurs within as short as 400 fs, a bleaching peak appears in 500-700 nm and an excited state absorption band at 470 nm. This suggests the HfN contains many free electrons and has effective e-e scattering. After this short period, a stable (ns lifetime) linear-like distribution forms in the TA spectrum,
from 450-750 nm. This linear-like distribution takes several nanoseconds to relax back to the steady state absorption levels. Figure 4 shows the exponential fitting of the time evolution at 470 nm with exponential fitting obtaining a lifetime of 1.7 ns.

5. Conclusion
Preliminary evidence from ultrafast transient absorption spectroscopy has shown evidence of long carrier lifetimes, on the order of nanoseconds in the material hafnium nitride. It is hypothesised the long relaxation times are due to the large mass difference between the constituent atoms of HfN leading to a large gap between the optical and acoustic branches in the phonon dispersion. The gap in the phonon dispersion in HfN reduces carrier thermalisation rates by removing phonon decay pathways creating a phonon bottleneck effect allowing electrons to reabsorb optical phonons. Materials which exhibit extremely slow carrier thermalisation rates can be used for the development of the Hot Carrier solar cell which can theoretically achieve very high power conversion efficiencies.

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References
[1] Shockley W and Queisser H J, 1961 Journal of Applied Physics 32(3) 510
[2] Hirst L C and Ekins-daukes N J, 2011 Progress in Photovoltaics: Research and Applications 19(3) 286
[3] Ross R and Nozik A, 1982 Journal of Applied Physics 53(5) 3813
[4] Würfel P, Brown A S, Humphrey T E and Green M A, 2005 Progress in Photovoltaics: Research and Applications 13(4) 277
[5] Green M A, 2003 Third Generation Photovoltaics: Advanced Solar Energy Conversion. Springer-Verlag Berlin and Heidelberg GmbH & Co. KG. ISBN 9783540265627
[6] Fröhlich H, 1954 Advances in Physics 3(11) 325
[7] Klemens P, 1966 Physical Review 148(2) 845
[8] Ridley B, 1996 Journal of Physics: Condensed Matter 8 L511
[9] Combeer G, König D, Green M and Guilleminoles J, 2008 Thin Solid Films 516(20) 6948
[10] Saha B, Acharya J, Sands T D and Waghmare U V, 2010 Journal of Applied Physics 107(3) 033715