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Nanosecond long excited state lifetimes observed in hafnium nitride

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ABSTRACT

Increasing photovoltaic conversion efficiency by overcoming the fundamental loss mechanisms due to hot carrier thermalisation remains one of the challenges in solar energy research. A large proportion of dynamic energy is lost due to thermalisation where hot carriers lose their energy to lattice vibrations within picoseconds. Extending hot carrier lifetimes will potentially improve the efficiency of photovoltaic devices. In this study, the bulk hafnium nitride film is proposed as a potential hot carrier absorber from its phononic properties. Hafnium nitride thin films were deposited by sputtering on quartz substrates. The films are polycrystalline as determined from X-ray diffraction and from X-ray photoelectron spectroscopy the chemical composition of the films are estimated to be $HfN_{0.9}$. The absorption coefficient of the film exhibits strong amplitude below 500 nm and free electron absorption at longer wavelengths. Transient absorption spectroscopy was used to investigate carrier dynamics in the visible and near-infrared spectral regions. For the first time we present evidence of up to nanosecond long lifetimes of photo-excited carriers observed in hafnium nitride. We propose that the long lived excited states are due to restricted phonon decay pathways in hafnium nitride. The long lived excited states in the bulk hafnium nitride film provide a simple route to devices designed to utilise hot carriers efficiently.

1. Introduction

The performance of conventional photovoltaic devices is limited by what is known as the Shockley-Queisser limit [1]. This limit relates the energy balance of a single junction photovoltaic device to the obtainable efficiency. From this analysis there are two fundamental loss mechanisms limiting the conversion efficiency of single junction solar cells to approximately 33%. The two majority loss mechanisms which reduce the power conversion efficiency by over 50% are in the form of thermalisation losses and non-absorbance of photons with energies below the semiconductor bandgap [2]. 'Hot carriers' is a term used to describe carriers that have energies above that of the bandgap of a semiconducting material. Thermalisation losses from hot carriers occur when carriers relax to the conduction band edge from elevated energy levels. This process occurs via emission of optical phonons from hot carriers. The optical phonons subsequently decay into acoustic phonons where energy is lost as heat and is irretrievable.

A hot carrier solar cell (HCSC) is a device which can potentially overcome these fundamental loss mechanisms [3–7]. The aim of the HCSC is to extract the hot carriers before their excess energy is lost through thermalisation processes, which occur on the time scale of several picoseconds at room temperature [8]. Two key requirements for the absorber layer in the HCSC is the ability of the material to maintain a hot carrier population sufficiently long enough for the extraction of hot carriers and a low bandgap to absorb the maximum amount of photons. Theoretically, HCSCs with a zero bandgap absorber are the most efficient provided hot carriers are collected at an elevated energy level [9]. A method proposed to meet the requirement for long hot carrier lifetimes is the use of a material where the phonon decay pathways are suppressed such that optical phonons can re-scatter their energy back to electrons [10]. Phonon decay can be suppressed if there is a large enough gap between the minimum of the optical branch and the maximum of the acoustic branch in the phonon dispersion such that no phonon decay from optical to acoustic phonons can occur due to energy and momentum conservation laws [11,12]. The hot carrier thermalisation time constant must be in the range of several hundred picoseconds in order to achieve efficiencies greater than that of the Shockley-Queisser limit [13,14]. To compete with existing tandem solar cells the thermalisation time must be further extended into the nanosecond range.

Hafnium nitride is part of the class of transition metal nitrides which has the potential to be used as a HCSC absorber [15]. The electrical conductivity of these transition metal nitrides varies from metallic to semiconducting and insulating depending on chemical composition [16]. Properties of group-IV transition metal nitrides have also led to research for applications for diffusion barriers, buffer layers in micro-

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electronics, thermoelectric and plasmonic technologies [17–20]. NaCl-structured HfN is metallic and is commonly deposited using physical vapour deposition techniques such as sputtering [21–23]. HfN has been grown with high crystalline quality on silicon and epitaxially on MgO substrates [24–26]. The electronic structure, phonon and optical properties have been calculated from first principle calculations [17,27,28]. The electronic structure of HfN is metallic with an continuous electron density of states and several electronic bands crossing the Fermi level. However, at the Gamma point there exists semiconductor-like bands where there are parabolic bands allowing for direct transitions at the Brillouin zone centre. A large phonon band gap is calculated for HfN due to the large mass difference between its constituent atoms [17]. Due to this HfN is expected to exhibit long hot carrier decay lifetimes. The large gap between the optical and acoustic phonon modes has been experimentally supported from inelastic neutron scattering experiments [29,30]. Raman scattering experiments have also shown this large gap between the optical and acoustic phonon modes [15,31]. The optical properties of HfN have been studied from transmission and reflection spectroscopy, from this its optical constants have been calculated [32,33]. While the electronic and optical properties have been previously studied for HfN the carrier dynamics are still largely unknown.

In this paper we report carrier dynamics of HfN films studied by ultrafast pump-probe transient absorption (TA) spectroscopy. The films were grown by reactive DC sputtering of a hafnium target. The film's structural and chemical properties were investigated by X-ray diffraction and X-ray photoelectron spectroscopy. The optical properties were investigated by an integrating sphere spectrophotometer. The investigation provides evidence of nanosecond long lifetimes of hot carriers in HfN. It is suggested that restricted phonon decay pathways in HfN play a role in the long lifetimes. The slowed hot carrier cooling in the bulk HfN film provides a simple route to devices designed to utilise hot carriers efficiently.

2. Experimental

2.1. Thin film deposition

Thin films of HfN were deposited on quartz substrates using an AJA ATC-2200 magnetron sputtering system by DC sputtering of a 4-in. hafnium 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 6 sccm was used. Before the deposition the chamber was pumped down to a base pressure of lower than 2.5×10^{-7} Torr. The samples were deposited with constant DC power of 100 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 h. The substrates were chemically cleaned using RCA1 and RCA2 solutions, rinsed in deionized water and blown dried with nitrogen gas just prior to loading into the load lock chamber. The hafnium sputter target was sputter cleaned for, at least 10 min, to remove surface oxides and other impurities prior to loading the samples from the load lock to the main chamber. Prior to the film deposition, the substrates were thermally degassed at 550 °C at the base pressure of 2.5×10^{-7} Torr for 1 h.

2.2. Characterisation

The films deposited were polycrystalline, NaCl structured with HfN (100) grains sizes of ~11 nm, as shown by X-ray diffraction measurements (Fig. S1, Supplementary Information). The chemical binding energies of Hf and N were shown to be in agreement with previous studies by X-ray photoelectron spectroscopy [34,35]. Analysis of the X-ray photoelectron spectra yielded an N/Hf ratio of the film of 0.9 (Fig. S2, Supplementary Information). However, the nitrogen content was expected to be underestimated due to preferential sputtering of nitrogen while preparing the sample surface for X-ray photoelectron measurements as seen in other transition metal nitrides such as tantalum nitride [36].

The film thickness was measured using a Dektak surface profilometer after selectively etching portions of the HfN film deposited on silicon with a buffered oxide etch solution. The transmission and reflection of the HfN thin film deposited on quartz were measured using a 150-mm integrating sphere with a PerkinElmer LAMBDA1050 UV/Vis/NIR spectrophotometer.

The femtosecond TA experiments were performed on the HfN samples with a TA spectrometer (Ultrafast Systems Helios). The laser system consisted of a Ti:sapphire oscillator (Tsunami), which seeded a regenerative amplifier (Spectra Physics Spitfire). The output of the amplifier was centered at 800 nm with a repetition rate of 1 kHz and pulse duration of 100 fs, which was then split into pump and probe beamlines. The 400 nm pump pulses were generated using a BBO crystal. The incident pump fluence was 60 μJ/cm^2 in the visible and 100 μJ/cm^2 for the near infrared. The probe beam passed through a delay stage and was used to generate a white light continuum in either 2 or 13 mm sapphire for the visible or near-infrared regions, respectively. The probe passed through the sample and a spectrometer, and then was detected by a CMOS CCD detector. The probe polarization was oriented at magic angle (54.7°) with respect to the pump polarization.

3. Results and discussion

3.1. Optical properties of HfN

Steady-state optical properties of the HfN thin film was measured with an integrating sphere spectrophotometer. Fig. 1 shows the absorption coefficient, α calculated from the approximation, $\alpha \approx -\frac{1}{d}\ln(\frac{T}{1-R})$ where d, is the film thickness which was measured to be approximately 60 nm. The inset of Fig. 1 shows the measured reflection and transmission spectra of the film used to determine the absorption coefficient. The reflection spectrum shows a minimum at 395 nm while the transmittance has a maximum at 480 nm. The transmittance does not reduce to zero at long wavelengths showing the metallic nature of the material where there is free carrier reflection and absorption of low energy photons. Strong absorption is evident at low wavelengths from interband transitions, while at long wavelengths there is absorption due to free carrier absorption. The region at wavelengths longer than the absorption minimum is characteristic of free electron absorption from Hf 4*d* states through intraband transitions [27]. There is free carrier absorption from ~500 nm onwards but the reflectivity is also large in this region. The absorption and reflection by free electrons in the material is indicative of the metallic nature of HfN.

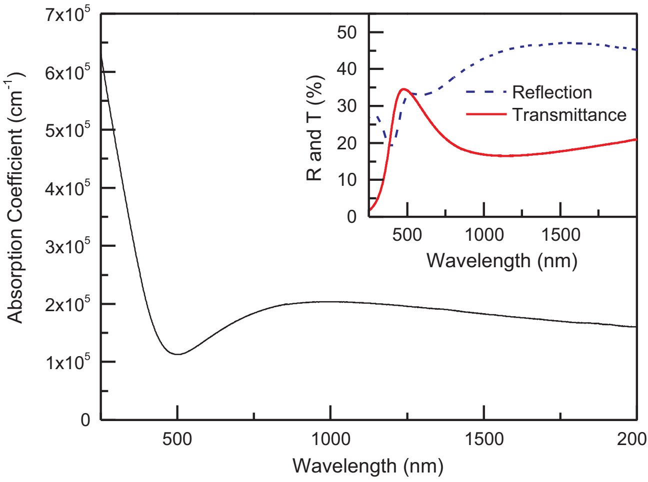

Fig. 1. Absorption coefficient of an HfN film deposited on a quartz substrate as a function of wavelength. Transmission and reflection spectra are shown in the inset.