



An Aluminum Nitride-based chemical sensor using Q-DLTS

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ARTICLE INFO

Article history:

Received 18 July 2011

Received in revised form 5 January 2012

Accepted 10 January 2012

Available online 16 January 2012

Keywords:

Aluminum Nitride

Termination

Q-DLTS

Sensor

ABSTRACT

The wide band-gap semiconductor material, single crystal Aluminum Nitride (AlN), was used in the development of a chemical sensor based on the Quantum Fingerprint™ method. The carefully prepared AlN surface was interrogated following exposure to test vapors of various species using a Charge-based Deep Level Transient Spectroscopy (Q-DLTS) instrument to analyze the presence of surface charge states induced in the band-gap by adsorbed vapor molecules. The AlN was metallized with a titanium adhesion layer topped with a gold contact layer. This produced a contact with Schottky-like properties. The AlN surface was terminated with hydrogen and was tested for its responses to water vapor, several alcohols, ethyl acetate, toluene, and chloroform in a small enclosure. The effect on the Q-DLTS spectrum was compared in each case to the baseline spectrum obtained prior to the testing exposure. All Q-DLTS spectra were observed to return to the preceding spectrum background upon removal of the test vapor. Spectral differences were observed that allowed discrimination to be made between the species tested. The number of peaks varied between one and three and their locations spanned the entire available spectral range. Combinations of the peak locations, amplitude, and amplitude ratios may be used to discriminate between different species.

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1. Introduction

Aluminum Nitride (AlN) is a wide band-gap semiconductor with a band-gap of 6.28 eV and is an appealing material for electronic packaging applications due to its ability to operate at high temperatures, its superior hardness, and its resistance to chemicals [1,2]. AlN, like other wide band-gap materials, may be used in the fabrication of Quantum Fingerprint™ sensors. The Quantum Fingerprint™ sensor is fabricated using a metallized wide band-gap semiconductor substrate with an electrostatic thin film at the surface where adsorbed molecules from the ambient environment create surface states or modify existing trap configurations which may be observed through the use of a Charge-based Deep Level Transient Spectroscopy (Q-DLTS) device [3,4]. Sensors of this type have previously been created using Diamond-Like Carbon (DLC) films and were used to detect water vapor [5]. The construction of a database of sensor-specific Q-DLTS responses would eventually allow for identification of unknown materials.

The single crystal AlN-based Quantum Fingerprint™ sensors studied here utilized a single gap between two symmetrical Schottky metallized contacts on a single polished, cleaned, and prepared surface. Chemicals that adsorb onto the surface of the AlN have the ability to create surface defects that acquire the role of surface traps [6,7]. These traps were filled by the Q-DLTS device via an initial filling

voltage pulse and were then observed as the trapped charge decayed away. Each trap emission has a characteristic emission rate which is identified by the Q-DLTS device. The maximum emission rate is characterized by a peak in the Q-DLTS spectrum. Multiple emission rates may exist for each sensor resulting in multiple peaks in the Q-DLTS spectrum. The sensor surface may be altered to create an electrostatic thin film in order to alter the electron affinity of the surface and thereby change the ability of the sensor to detect certain chemicals. This was accomplished in the current work using hydrogen plasma. Hydrogen surface termination via plasma exposure is an established method used in the termination of other wide band-gap semiconductors [8].

The finished sensors were exposed to vapors of methanol, ethanol, propanol-1, ethyl acetate, toluene, chloroform, and water in a small enclosure. In each case, after a short period of time, changes observed in the Q-DLTS spectra reached a maximum, indicating that equilibrium between adsorption and desorption processes had been achieved. The time needed to reach equilibrium varied between vapor types. The Q-DLTS background measurements made prior to exposure were subtracted from the data, to yield spectra due solely to exposure to the test vapors. Background corrected Q-DLTS spectra for all vapors were compared.

2. Experimental

The AlN Quantum Fingerprint™ sensor was fabricated using a single crystal AlN substrate. The surface was cleaned with a series of aqueous cleaning steps designed to remove potential contaminants

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that affect metallization contact quality, such as: oxides, metals, and organic films. The sample was subsequently metallized using thermal resistive evaporation. Two parallel contacts were metallized on the polished surface, leaving a 1.0 mm bare gap between contacts. The metallization recipe used was a titanium adhesion layer with a gold capping layer (100 nm/100 nm). Following this step, the sample was annealed in a helium atmosphere at 825 °C for a period of five minutes to promote adhesion and enhance the electrical contact. Current–voltage (I–V) measurements were taken after annealing to analyze the contact quality and characteristics. Following this, the sensor was exposed to a hydrogen plasma derived from Scott Specialty Gas high purity 5% hydrogen gas/95% argon gas mixture for a period of 10 min on the medium power setting in the Harrick Plasma PDC-32G plasma cleaning device. Prior to termination, the chamber was flushed three times to remove any ambient gas in the chamber. I–V measurements are taken to observe the change in the surface characteristics resulting from hydrogen termination. A more detailed description of the fabrication methods of this sensor may be found in a separate publication [9].

The completed sensor was placed in a 150 ml aluminum chamber with feedthroughs for electrical leads. The chamber provided the ability to contain the vapors under investigation as well the ability to shield for ambient 60 Hz and high frequency noise that would greatly affect the sensitive Q-DLTS measurements. A background Q-DLTS measurement was generated prior to exposure to vapors under investigation. At ambient temperatures, 1 ml of each material to be tested was put in the bottom of the chamber before being sealed. The materials under investigation were the vapors of ethanol, methanol, propanol-1, ethyl acetate, toluene, chloroform, and water. Measurements were taken at five minute intervals and each sample was averaged 10 times to reduce any noise. Leakage currents were compensated with an input bias current compensation sub-circuit. The voltage filling pulse duration was set at 100 ms to investigate traps in the Q-DLTS spectrum without the introduction of large amounts of leakage common with longer filling pulses. Sampling was delayed 5 μ s to allow for the decay of switching transients in the Q-DLTS hardware. Sampling duration was 1000 ms and the sampling rate was 250,000 samples per second, the maximum for this system. The operation and design of this system are discussed in greater detail in an alternate publication [10].

Q-DLTS measurements were performed at five minute intervals until the spectrum ceased evolving. The background Q-DLTS measurement was subtracted from the final equilibrium Q-DLTS spectra to determine the net change resulting from the exposure to vapors. The background corrected spectra from the range of materials were then compared. In between measurements, the chamber was opened and any remaining liquid and vapor was removed. The chamber remained open for a minimum of 15 min and heated to approximately 50 °C in order to ensure that all adsorbed vapors from the prior test were removed. This was verified by analyzing the background spectra taken before measurements for inconsistencies.

3. Theory

The Quantum Fingerprint™ sensor employs a new method for species detection and identification compared to established sensing techniques. A semiconductor contains a band structure that may be divided into three regions: the valence band, conduction band and band gap [11]. In the band-gap, electron traps may occur and this is the most important characteristic of the semiconductor that is exploited by the Quantum Fingerprint™ method [12]. An electrostatic thin film on the surface of a semiconductor has the ability to attract chemical species [3]. These attracted species create surface defects that acquire the role of surface traps [6,7]. There are a finite number of available sites per unit surface area for the adsorption process to occur. This adsorption process may be a result of physisorption or

chemisorption. If an activation energy is needed for a chemisorption process, in the case of activated adsorption, the chemisorption process occurs slowly and as a consequence an equilibrium between adsorption and desorption is established slowly. An equilibrium is reached when the adsorption rate is equaled by the desorption rate. A maximum Q-DLTS peak is observed at this time.

Prior studies have been undertaken to characterize the existing bulk trap structure of single crystal AlN using alternative techniques [13,14]. Two existing bulk traps were observed by Soltamov et al. using electron paramagnetic resonance (EPR) and thermoluminescence (TL), which were attributed to oxygen at the N-site and/or silicon at the Al-site. Polyakov et al. also characterized two electron traps with ionization energies of 0.26 eV and 0.65 eV and concentrations of 10^{13} cm^{-3} and 10^{15} cm^{-3} , respectively. These two traps, and potentially others, will comprise a background signal for the Q-DLTS spectra.

Q-DLTS measurements are most sensitive at the surface of a semiconductor, making this technique ideal for this type of analysis [15]. According to Lang's original DLTS method [16], the Q-DLTS technique relies on cyclic bias pulses to momentarily excite the traps of p - n junctions and Schottky barriers. The electron occupation of the level is monitored as it returns to thermal equilibrium by measuring the associated charge transients. The charge transient is measured at two different times (t_1 and t_2), which is termed the "rate window" and the difference, $Q(t_2) - Q(t_1)$ is plotted versus the rate window. According to Maxwell–Boltzmann statistics, the thermal emission rates are strongly dependent upon temperature and at a particular temperature, a peak may be produced in the spectrum because $Q(t_2) - Q(t_1)$. Further details on the operation of the Q-DLTS device may be found in prior publications [10,17].

The emission rate, e_n for the electrons that are trapped has the form: [18]

$$e_n = \sigma \Gamma_n T^2 \exp\left(-\frac{E_a}{kT}\right) \quad (1)$$

where σ is the capture cross section, T is the temperature, E_a is the activation energy, k is the Boltzmann constant, and Γ_n is defined as:

$$\Gamma_n = 2\sqrt{3} \left(\frac{2\pi}{h^2}\right)^{3/2} k^2 m_n \quad (2)$$

where h is the Planck constant and m_n is the effective mass of the electron. The equations for holes are analogous. Due to the Arrhenius dependence of the emission rate, characteristic information for σ and E_a can be calculated using Eq. (1) through a variation in the temperature of the sample. Arrhenius data was not generated in the course of this research because it was critical to maintain a constant temperature in the chamber. Changes in temperature change the vapor pressure and affect the equilibrium between adsorption and desorption. This in turn changes peak amplitudes observed in the Q-DLTS, potentially perturbing Arrhenius results.

Surface traps that are excited through introduction of the filling pulse in the Q-DLTS process will emit charge at a characteristic rate when using a parallel contact metallization scheme. It is possible for each species adsorbed onto the surface of the semiconductor to have multiple orientations. Different orientations would provide multiple characteristic traps, each with different amounts of charge and different charge emission time constants, for a single species. In this way, a single species may distinguishable from another based on its charge emission signature or "fingerprint". The surface of the semiconductor may also have dangling bonds that are capable of being terminated. By terminating these dangling surface bonds electron affinity may be increased, providing an attractive layer to polar molecules.

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