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Annealing improvement on the localized states of plasma grown boron nitride film assessed through admittance measurements

Orhan Özdemir^{a,*}, Mustafa Anutgan^b, Tamila Aliyeva-Anutgan^b, İsmail Atilgan^b, Bayram Katircioğlu^b

^a Yildiz Technical University, Physics Department, Davutpaşa, İstanbul, Turkey ^b Middle East Technical University, Physics Department, Balgat, Ankara, Turkey

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ABSTRACT

Boron nitride (BN) thin film was grown by plasma enhanced chemical vapor deposition (PECVD) technique and was investigated by UV–Visible transmission, Fourier transform infrared (FTIR) and ac conductance spectroscopies. Mainly the density of electronic localized states (D_{it}) at BN/Si interface was obtained by continuum and statistical models of ac conductance through an MIS structure (Al/BN film/Si). The origins of the electronic defects have been outlined and discussed within the frame of a nitrogen deficient turbostratic structure where more or less parallel hexagonal crystallites of distributed size would be embedded in a disordered phase. The nitrogen deficiency of the film was tried to be restored by annealing treatment under nitrogen atmosphere at two temperatures.

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1. Introduction

The boron nitride compound (BN) is a polymorphous material. Its most stable and natural phase being hexagonal form (h-BN) is relatively easier to deposit in thin film form by plasma enhanced chemical vapor deposition (PECVD) system which is widely used for production of large area low cost opto-electronic materials [1]. In addition, h-BN film is a potential material for thin film opto-electronic applications [2]. Its possible negative electron affinity (NEA) allows some applications like displays, detectors, electron microscopes, cold cathode emitters etc. [3,4]. Moreover, its chemical inertness and dielectric behavior render it a candidate for passivation or insulator layer in both VLSI circuits assigned to reactive media and high-speed integrated circuits of the metal–insulator–semiconductor structure [5–9].

h-BN films grown by PECVD upto nowadays are very defective [1,10]. Huge density of localized electronic states (DOS), some of which are related to the stoichiometric problems, constitutes a serious threat to the possible applications of h-BN films despite their low cost and easy production. These localized states are studied by admittance measurements on a device involving the film under

investigation [11,12]. For that purpose, metal-semiconductor (MS) and metal-insulator-semiconductor or metal (MIS or MIM) devices must be available for simplicity of both production and interpretation of the measured data.

The charges of the localized states within h-BN film may be changed by storing free charge carriers on the electrode by applying externally dc and ac bias voltages on MIM and MIS structures. These charges are followed by admittance measurements (both capacitance and conductance components). MIM structure has the advantage over MIS one in its ability to measure exclusively the geometric capacitance of the dielectric film, avoiding the contribution of the semiconductor; this geometric capacitance may be used to obtain the film thickness if its dielectric constant is known or vice versa. On the other hand, MIS structure is preferable over MIM one since the second electrode (semiconductor) may constitute a reference for determining the charge state of the system at flat band voltage (V_{FB}). The capacitance C_{FB} corresponding to this reference voltage $V_{\rm FB}$ may be determined experimentally and the amount of charges in the film (bulk and surface) is then evaluated from $V_{\rm FB}$. The Fermi level of the semiconductor may scan an energy interval corresponding approximately to its half gap (here for p-type silicon) from midgap to about the valence band edge by changing the gate electrode voltage, $V_{\rm G}$. Consequently, the distribution of DOS may be obtained along this energy interval.





^{*} Corresponding author. Tel.: +90 212 383 4279. E-mail address: ytu.orhan@gmail.com (O. Özdemir).

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In this work, mainly an MIS structure was used since BN film is relatively resistive and then may be taken as a dielectric. The admittance measurements are utilized in the analysis of DOS in BN films deposited on p-type silicon crystal. In this frame, the continuum model [12] was first used for retrieving the DOS at the BN film/Si interface. The statistical model was parallelly used for determining whether or not the interface local charges are inhomogeneously distributed [12].

2. Preparation and measuring tools

Two (100) oriented p-type silicon wafers (50 and 2Ω cm) for FTIR and the admittance analyses, respectively, were cleaned with standard RCA (Radio Corporation of America) cleaning procedure. Quartz plates, glass and aluminum (Al) coated glass microscope slides (cleaned by boiling in degreasing agent and dipping in diluted hydrogen peroxide (H₂O₂) and trichloroethylene (TCE) solution) were used as substrates for UV-Visible transmission, mechanical thickness and admittance measurements, respectively. Prior to placing the substrates on the grounded lower electrode of PECVD system (µP 80, Plasmalab), backside of the substrate for MIS structure was coated by Al and the sample was annealed in nitrogen ambient at 530 °C to form ohmic contact, followed by front side cleaning via floating on diluted hydrofluoric acid (HF) solution. Then, BN film was deposited by 13.56 MHz PECVD technique, using $0.55 \text{ W/cm}^2 \text{ RF}$ power, flow rates of $20 \text{ cm}^3/\text{min}$ ammonia (NH₃) and 4.5 cm³ diborane (B₂H₆, diluted 15% in Hydrogen, H) under pressure of 0.5 Torr at 300 °C. After deposition, Al as gate electrode was evaporated through a shadow mask of diameter 0.15 cm to fabricate MIS (Al/BN/p-c-Si/Al) and MIM (Al/BN/Al coated glass) structures, respectively. The thickness of BN film is determined as 375 nm by a profiler (Ambios XP-2), and hence deposition rate is determined to be 4.2 nm/min. The film was annealed under nitrogen atmosphere for 90 min at two different temperatures (475 and 650°C).

By means of optical transmission measurements obtained by a UV–Visible spectrometer (λ 2S, PerkinElmer), refractive index (n), optical energy gap of the film (E_G), and characteristic energy width of the tail states (=Urbach energy, E_0) were obtained. On the other hand, measurement of IR spectrum (FTIR, Nicolet 520) gives information on the film structure since each phase of BN gives distinct vibrational absorption spectrum. Finally, distributions of localized DOS, main contribution of this work, were investigated via admittance spectroscopy performed by an LCR meter (HP 4192A) within a frequency range from 3 kHz to 100 kHz through the MIS structure.

3. Results

3.1. Optical characterization

Optical transmittance measurements were taken in the UV–Visible region (200–1100 nm) as depicted in Fig. 1. The optical path, *n*·*d* of the light within the BN films was deduced from the fringes of the transparent region of the transmittance spectrum. Then, the refractive index, *n* was found by using the previously estimated thickness, *d* in the optical path. The refractive index was found about 1.75 and remaining almost the same after the annealing treatments. Moreover, coinciding $n (\approx \sqrt{\varepsilon} \text{ where } \varepsilon = \text{permittivity})$ was obtained as 1.78 when compared with the one obtained through capacitance–voltage (*C*–*V*) measurement at accumulation for the highest frequency, i.e., $C = \varepsilon A/d$ with A = electrode area. The absorption coefficient as a function of incident photon energy, $\alpha(h\nu)$ was calculated in the absorption region of the spectrum. The optical gap was found from the energy axis intercept of the linear fit in the $(\alpha h\nu)^{1/2}$ vs. $h\nu$ graph, adequate for disordered



Fig. 1. Transmission spectrum of as-grown BN film in the UV–Visible region. Inset (i) shows the corresponding $(\alpha h v)^{1/2}$ and $\alpha h v$ vs. h v plots for the estimations of band gap E_g and Urbach energy E_0 , respectively. Weak absorption (a), medium absorption (b) and high absorption (c) regions are also indicated. Inset (ii) gives out E_g , E_0 and refractive index for the as-grown and 475 and 650 °C annealed samples.

semiconductors. The energy band gap slightly increases from 5.20 to 5.30 eV with increasing annealing temperature (Fig. 1). These values are close to the gap of h-BN [13]. Finally, the $log(\alpha h\nu)$ vs. $(h\nu)$ graph was plotted to see the degree of tail state density from the inverse slope of the linear fit (i.e., Urbach energy, E_0). E_0 is found to increase gradually from 0.17 towards 0.20 eV as annealing temperature increases (Fig. 1).

Infrared spectra of PECVD grown BN film is depicted in Fig. 2. In Fig. 2(a) peaks around 795 cm⁻¹ (B-N-B out-of-plane bending) and broad one around 1388 cm⁻¹ (B-N stretching) indicate that films at hand contain poorly crystalline hexagonal phase, i.e., turbostratic BN (t-BN) [14]. Broad peak at 1388 cm⁻¹ has a shoulder which may be assigned to B-O-N vibration mode [15]. Besides, with increasing annealing temperature B-O stretching mode around 1250 cm⁻¹ can be detected. In Fig. 2(b) it is clearly seen that with annealing, hydrogen evolves from the film. Using calibration constants for B–H and N–H bonds [16,17], a decrease of hydrogen content is calculated (inset of Fig. 2(b)).

3.2. Admittance analysis

Admittance spectroscopy consists of measuring capacitance, C_m together with conductance, G_m as a function of various parameters such as dc bias voltage V_G , ac voltage modulation frequency, ω . It has been extensively used for investigating the electronic properties of MIS structure due to its charge sensitivity. The measurements of C_m and G_m/ω of MIS (Al/BN film/Si) capacitor vs. V_G at room temperature under various ω are given in Fig. 3a. Before proceeding



Fig. 2. (a) B-N-B out-of-plane (*op*) bending and B-N in-plane (*in*) stretching modes: characteristic peaks of sp² phase. Possible oxygen containing modes are indicated. (b) Hydrogen containing bonds: B—H out-of-plane bending, B—H and N—H stretching. Inset shows the calculated hydrogen atom density as a function of annealing temperature.

further, let us resume the basic points of the admittance analyses considering both capacitance and conductance components for better seizing the proposed interpretations.

Three distinct regions are evident when $C_m - V_G$ measurement is performed: at high negative bias, accumulation of majority carriers is formed at the interface (holes for p-type silicon) and this dc bias independent capacitance value C_{BN} is used to obtain the insulator film geometric capacitance after correcting the eventual effect of series resistance (R_s) . When applied gate bias is reduced (i.e., dc gate bias scanned from accumulation towards more positive values), the bias dependent capacitance region defines the second bias regime as depletion. Further change of dc gate bias towards more positive values accumulates minorities at the interface and forms the third bias independent capacitance region, namely inversion. The inversion capacitance in this work, as given in Fig. 3a, remains below the accumulation one since, despite the availability of minorities at the interface for dc bias, their ac modulation does not occur within the 3-100 kHz frequency interval, due to relatively lower generation/recombination rates of the minorities; instead the required ac charge modulation occurs at the depletion edge and the overall capacitance is the series combination of the film and silicon depletion capacitances.

From the accumulation to the depletion, the polarity of silicon band bending $q\psi_s$ changes, being flat ($\psi_s = 0$) at $V_G(\equiv V_{FB}) = 0$ for ideal structure. However, in practical conditions, $V_{FB} \neq 0$, due to the existence of localized charges both in the bulk of the dielectric (Q_f) and at the interface (Q_{it}) apart from a negligibly small effect of work function difference between gate metal and silicon materials. In other words, these charges shift the $C_m - V_G$ curves along the voltage axis. Consequently, the determination of V_{FB} is crucial for the overall evaluation of local charges. From the magnitude of the flatband shift of $C_m - V_G$ curve, roughly the effective density of charges located within the film and/or at the film/substrate interface can be estimated [11,12,18,19]

$$Q_{\rm it} + Q_{\rm f} \approx V_{\rm FB} C_{\rm BN} \tag{1}$$

Although C_m and G_m/ω branches of the measured admittance $Y_m(=G_m + j\omega C_m)$ may be equally used for extracting interface state density, the conductance component is preferable since it is more accurate and sensitive due to its peak behavior. However, interface conductance effects are not detectable in the accumulation and strong inversion regions due to the large amount of stored charge carriers. Conductance peaks along the depletion region, due to the exchange of majority carriers of low quantity, between the interface localized states and the relevant band are preferable for easiness of interpretation (here, the conductance is due to the time delay existing between the demand and supply of the majority carriers during the exchange).

The interface trap admittance $Y_p(=G_p + j\omega C_p)$ and specially G_p/ω may be retrieved from the experimentally measured admittance $Y_m(=G_m + j\omega C_m)$, first, by removing the contribution of both the dielectric film capacitance, C_{BN} and the series resistance, R_s according to the equivalent circuit given in Fig. 3b. For that purpose, the expressions of C_{BN} and R_s are deduced from the high frequency measured accumulation admittance $Y_{ma}(=G_{ma} + j\omega C_{ma})$ (which is approximately the inverse of the series combination of these two impedances ($1/j\omega C_{BN}$) and R_s [12]):

$$\frac{G_{\rm p}}{\omega} = \frac{\omega C_{\rm BN}^2 (G_{\rm m} - \omega^2 C_{\rm m}^2 R_{\rm s} - R_{\rm s} G_{\rm m}^2)}{(\omega^2 C_{\rm BN} R_{\rm s} C_{\rm m} - G_{\rm m})^2 + \omega^2 (C_{\rm BN} - C_{\rm m} - C_{\rm BN} R_{\rm s} G_{\rm m})^2}$$
(2)

with $R_{\rm s} = G_{\rm ma}/(G_{\rm ma}^2 + \omega^2 C_{\rm ma}^2)$ and $C_{\rm BN} = C_{\rm ma}(1+(G_{\rm ma}/\omega C_{\rm ma})^2)$.

The retrieved G_p/ω vs. dc gate voltage and frequency curves are given in Fig. 3c and d respectively.



Fig. 3. (a) Admittance (C_m and G_m/ω) as a function of gate bias (V_G) at room temperature on both Al/BN/p-Si/Al MIS and Al/BN/Al MIM structures, respectively. (b) Equivalent circuit used for retrieving the interface state density D_{it} . (c) G_p/ω as a function of V_G for various time frequencies after insulator film capacitance (C_{BN}) and series resistance (R_s) compensation. (d) G_p/ω vs. time frequency f for several bias voltages (corresponding to the depletion and onset of weak inversion regimes) after insulator film capacitance (C_{BN}) and series resistance (C_{BN}) and series resistance (R_s) compensation.

The localized electronic states around the BN/Si interface should be distributed throughout the BN energy band gap as outline in Section 4. When ac gate voltage modulation is applied for admittance measurement, a modulation of the Fermi level position at the interface will be induced between *E* and *E* + d*E* and then the occupancy of a certain amount $D_{it}(E) dE$ of interface traps is affected with $D_{it}(E)$ = number of interface traps/(area energy). This leads to the following expression of G_p/ω for the so-called continuum model:

$$\frac{G_{\rm p}}{\omega} = \frac{q^2 D_{\rm it}}{2\omega \tau_{\rm p}} A \ln(1 + \omega^2 \tau_{\rm p}^2) \tag{3}$$

where τ_p^{-1} = hole emission/capture time = $\sigma_p v_{th} N_A \exp(q \psi_s / kT)$ with σ_p = trap capture cross section, v_{th} = thermal velocity, N_A = majority doping density, ψ_s = silicon interface band bending. $D_{it}(E)$ around the interface level *E* may be evaluated from G_p / ω peak value:

$$D_{\rm it} = \frac{\left(G_{\rm p}/\omega\right)_{\rm max}}{0.402q^2A} \tag{4}$$

The energy distribution of $D_{it}(E)$ may be obtained by changing the gate voltage V_G along the depletion region where the probe trap energy E_T , defined by the interface Fermi level E_F and measured from the valence band edge E_V as ΔE is scanned from the midgap



Fig. 4. Distribution of effective density of states (D_{it}) along the half energy gap of Si obtained by continuum and statistical ac conductance models: for as-grown (open and filled circles) and annealed (open and filled rectangle) at 475 and 650 °C (open and filled triangular) films, respectively.

to the proximity of valence band edge:

$$\Delta E = E_{\rm V} - E_{\rm F} = q\psi_{\rm S} + kT \ln(N_{\rm A}/n_{\rm i}) \tag{5}$$

where n_i = silicon intrinsic carrier concentration. Here ψ_s and N_A are evaluated from the measured high frequency $C_m - V_G$ curve with $C_m = C_D C_{BN}/(C_D + C_{BN})$; $C_D = \varepsilon_s A/W$; $\psi_s = q N_A W^2/2\varepsilon_s$; W = depletion width. The experimentally determined distributions of $D_{it}(E)$ are reported in Fig. 4.

If the eventual traps are inhomogeneously distributed throughout the interface plane, the above continuum model supplies wrong $D_{it}(E)$ values since an inhomogeneous distribution of interface traps would lead to a distribution of interface silicon band bending ψ_s . The statistical model was developed taking into account this phenomenon where a Gaussian distribution $P(\psi_s)$ of ψ_s around its average $\langle \psi_s \rangle$ was assumed with σ_s being the variance of band bending in terms of kT/q [12] and G_p/ω turns into $\langle G_p \rangle/\omega$:

$$\frac{\langle G_{\rm p} \rangle}{\omega} = q^2 D_{\rm it} f_{\rm D} A(\sigma_{\rm s}) \tag{6}$$

with

$$f_{\rm D}(\sigma_{\rm s}) = \frac{\left(2\pi\sigma_{\rm s}^2\right)^{-1/2}}{2\xi} \int_{-\infty}^{+\infty} \exp\left(-\frac{\eta^2}{2\sigma_{\rm s}^2}\right) \exp(-\eta)$$
$$\times \ln(1+\xi^2 \exp(2\eta)) \,\mathrm{d}\eta \tag{7}$$

where $\eta = u_s - \bar{u}_s$ (with $u_s = e^{q\psi_s/kT}$), $\xi = \omega \tau_p$ and ξ_p is the value of ξ corresponding to the maximum of the G_p/ω vs. ln ω curve.

From the experimentally obtained $\langle G_p \rangle / \omega$ vs. $\ln(\omega)$ curve (Fig. 3d), the ratio of two $\langle G_p \rangle / \omega$ values at two discrete frequencies (peak frequency ω_p and 5 ω_p or 1/5 ω_p for example [12]) is evaluated and this ratio is used to find σ_s by solving numerically the relation (7). Finally, D_{it} is determined from the relation (6) at the $\langle G_p \rangle / \omega$ vs. $\ln(\omega)$ peak for the gate voltage V_G at hand. $D_{it}(E)$ vs. E_T – E_V distribution is obtained (Fig. 4) by the same procedure, outlined previously for continuum model.

4. Discussion

The PECVD deposited BN film, at least a relatively thin interfacial layer, seems extremely defective as probed by the admittance spectroscopy. In this section, the structural origins of the electronic defects have been outlined and discussed.

4.1. Atomic configuration and energy band structure

One of the approaches for studying bonds is to consider the bonds as "molecular" orbitals which are "built" of overlapping atomic orbitals. Both for boron and nitrogen, 3 equivalent (hybrid) orbitals may be obtained by combining one 2s-orbital with two 2porbitals (planar $2p_x$ and $2p_y$) as three sp^2 hybrid orbitals (Fig. 5i). Three planar sp²-like σ bonds are formed around each of the components. An unhybridized free p_z atomic orbital remains on each component, which are perpendicular to the plane of the three sp² orbitals (Fig. 5iv). Due to the greater nuclear charge of nitrogen, the nitrogen orbital $(p_z)_N$ is lying lower in potential energy than that of the boron $(p_z)_B$. This is schematically depicted in Fig. 6d. Consequently, $(p_z)_N$ is expected to be occupied by two electrons (of opposite spin) and $(p_z)_B$ remains empty (it is assumed here that one of the 2s² electrons of nitrogen atom participates in sp² bonding, the other is excited to $(p_z)_N$ orbital). In other words, the B–N bond is slightly polar $(B^{+\delta} \underset{d}{\longleftrightarrow} N^{-\delta})$, leading to a finite dipole moment $\mu = d\delta$.

The possibility of double bonding in BN might be speculated as follows [20]. The two $(p_z)_N$ electrons around the nitrogen as shown in Fig. 5iv might be partially available for π -bonding, by the partial transfer of $(p_z)_N$ electrons to $(p_z)_B$ at the boron site, without totally compensating the transfer along the sp²- σ bond from boron to nitrogen due to the differences in electronegativity between boron and nitrogen. However, this double bond character could not be comparable to that of a carbon–carbon double bond [21]. Therefore, the sharing of nitrogen $(p_z)_N$ electron pair in the bond building remains limited and depicted in Fig. 5iv.

The above described boron–nitrogen combination where each component atom of one sort has three planar trigonal $sp^2-\sigma$ bonds 120° apart to three atoms of second sort, may easily lead to six sided planar ring structure.

These six-fold B₃N₃ rings have the ability to be arranged into a hexagonal 2-dimensional infinite layers which are held together by weak Van der Waals or dipolar interaction. As depicted in Fig. 5vi, these hexagons are packed directly on top of each other where a boron atom in one layer remains closest to each corresponding nitrogen atom in the neighboring layers with ABAB... sequence of planes. However, omitting the diatomic structure, sequence of hexagonal lattice is as AAAA..., exhibiting the second difference apart from the polarity of bonds from the packing of graphite where the hexagons are shifted by one bond length along the neighboring planes and leading to ABAB... sequence. The analysis so far establishes the theoretical basis of hexagonal boron nitride (h-BN) crystals. Experiments have carried out that h-BN is the only stable phase found in nature although BN may be forged in, more or less stable, polymorphous microscopic arrangements (i.e., rhombohedral, cubic, and wurtzite symmetries [22]) in the practical laboratory conditions.

Instead of the ideal single crystalline forms, the BN compound appears practically at various (or microcrystalline or nanocrystalline) structures. In this respect, the qualification turbostratic is commonly used where hexagonal crystallites of distributed sizes are embedded in a disordered phase. Each crystallite may be more or less perfect; most of them may contain a varying number of point defects such as vacancies or dangling bonds. When BN material



Fig. 5. Schematic illustration of BN atomic organization from atomic orbitals to a turbostratic structure.

is produced in thin film form at low temperature without special precautions, a turbostratic structure is unavoidable [23]. Relatively far from the substrate, these sp²– σ bonded hexagonal BN planar crystallites, which are relatively defect free, can have random orientations (i.e., rotated more or less around *c*-axis). These layers of planar hexagonal grains may not be perfectly parallel to each other and the ABAB... sequence of layers might be no longer maintained. However, the "grain" boundary regions might be extremely defective (a typical diagram depicting the turbostratic structure is given in Fig. 6vii). The degree of porosity and contamination by impurities may, of course, depend on the production conditions and surroundings and then the resulting physical properties are affected. At the extreme limit, this turbostratic structure may be qualified as "amorphous" where the coherence length is reduced

to around the interatomic distance. During the film growth, at the initial stage, due to mainly the effects of substrate surface, the first layer on the substrate of thickness 2–3 nm may be amorphous. This layer might contain defects of all sorts leading to a huge density of electronic states which are expected to be distributed in energy from valence band to the conduction band.

The three dimensional tight-binding (TB) band structure for h-BN has been calculated [24] by transferring the TB interactions from the analogous and better understood graphite. The results are partially reported in Fig. 6a and b from ref. [24]. These figures are in reasonable agreement with the experimental electronic structure extracted from X-ray and photoemission measurements [24]. Contrary to the graphite without forbidden gap, h-BN exhibits a net direct gap at the Brillouin Zone (BZ) boundary along the



Fig. 6. (a) Composition of density of states around the band edges for both valence and conduction bands [24], (b) energy vs. quasimomentum along the indicated direction in the Brillouin Zone for both valence and conduction bands [24], (c) first BZ of h-BN structure (where energy gap occurs at the BZ boundary KPH [24]), and (d) schematic representation of atomic orbital interaction for producing both valence and conduction bands.

quasimomentum line KPH (Fig. 6c). Moreover, the valence band region around the maximum is eventually constituted by $(p_z)_N$ orbital dominant bonding π states, while the region of the conduction band around minimum is rather constituted by $(p_z)_B$ orbital dominant anti-bonding π^* states (Fig. 6a). This behavior might be qualitatively depicted in Fig. 6d.

4.2. Eventual distribution of localized states throughout the gap

In real cases (Fig. 5vii), there are unavoidable deviations from the ideal configurations leading to localized states, existing within limited regions of the material. These localized states may be roughly divided into two classes: (i) tail states and (ii) deep states. The energy levels of these states are expected to be distributed in energy due to the possible differences in the surrounding of each state.

(i) Bond angle and bond length distortions lead to a local trapping potentials, each one in its turn, localizes one of the band energy levels *E*, measured from the relevant band edge. The total num-

ber of states remaining conserved, the width of the density of states (DOS) of a band may be broadened more or less on either side depending on the strength of the local perturbations.

The overall amount of a trapping potential, reflecting the strength of local distortion, is related to the defect formation energy such that larger defect formation energy decreases the thermodynamical existence probability of this defect.

Consequently, the density of localized states, N(E) vs. E should decrease (probably exponentially) towards the energy gap as a tail from the relevant band edge, $N(E) = N_{edge} \exp(-|E|/E_0)$ with E_0 being the so-called Urbach energy, interpreted as disorder parameter. This is depicted in Fig. 7.

(ii) The coordination defect states, mainly related to the broken or dangling bonds (DB) constitutes a second family of deep traps. As the surrounding of each atomic site might be different in this randomly distributed hexagonal BN clusters (Fig. 5vii), the density of energy levels associated with these DBs of each component, exhibits Gauss-like distribution within the energy gap. In other words, the boron and nitrogen related two dif-



Fig. 7. Expected distribution of localized states across the (pseudo) gap of turbostratic or amorphous BN film.

ferent Gaussians are located near the conduction and valence bands respectively following the atomic orbital picture, shown in Fig. 6d. The eventual Fermi level should be pinned between these two distributions, defining the unoccupancy and occupancy of them respectively. Taking into account the amphoteric nature of each sort of DBs, the doubly occupied sites lead to a shifted Gauss-like DOS distribution due to the correlation energy. Thus, these DB distributions together with the localized DOS of weakened bonding (valence band tail) and anti-bonding states (conduction band tails) should cover the whole forbidden gap at least within defective "amorphous" layer neighboring the substrate.

4.3. Speculation about the experimental results

The gate voltage region where the strong frequency dependent capacitance steps and the corresponding $G_{\rm m}/\omega$ peaks occur, has been admitted as the depletion region (Fig. 3a). As the strong accumulation voltage region could not be reached, especially for high frequencies, due to the voltage limitation of the admittance meter at hand (-35 to +35 V), the amount of frequency dependence of its capacitance has not been clearly represented in Fig. 3a. Apart from the effect of the series resistance R_s , eventual charge injection from the semiconductor side into the depth of the dielectric would lead to a strong frequency dependence of the accumulation capacitance [11]. This possibility was tested by the capacitance measurement on the MIM (Al/BN/Al) structure. The result is shown in Fig. 3a. The slight frequency dependence, remaining after R_s correction, points out that the charge injection from the silicon into the BN film remains within a shallow thin region compared with the whole film thickness (less than 1% which corresponds to about 2-3 nm). This probable interlayer/facial layer, although relatively thin, should contain a very large density of localized charge states, extended throughout the energy gap (one possible origin of these defects was presented previously in Section 4.2). The detailed study of charge carrier injection in BN film will be the subject of the next work; but here a fragment of injection kinetics is reported in Fig. 8. In the MIS structure at hand, holes and electrons to be injected are stored at the interface by strong accumulation and inversion respectively. As predicted by the relation (1), the increasing amount of injected charges will gradually shift the whole $C_m - V_G$ curve along the voltage axis (negative side for hole injection, positive side for electron injection). The evolution of specific voltage (denoted as $V_{\rm HH}$) through C–V_G curves was monitored as follows: initially C–V curve was measured and fitted to cubic spline. A specific capacitance ($C_{\rm HH}$), corresponding to $V_{\rm HH}$, was defined as the middle value of accumulation and inversion capacitance due to practical reasons instead of the conventional flat band voltage, $V_{\rm FB}$. The measured



Fig. 8. Kinetics of the high frequency C_m vs. V_G shift under the stress of ± 10 V gate voltage. The whole C_m vs. V_G shift in time was followed by the gate voltage V_{HH} corresponding to the half value of the capacitance step.

 $V_{\rm HH}$ symbolizes the shift of whole C-V curve along the voltage axis and reflects the injected amount of charges into the BN film. For a very short time (less than 0.2 s.), voltage stress sequence was interrupted and the resulting C-V curve was fitted with cubic spline regression approach and the corresponding new $V_{\rm HH}(t)$ was determined and applied to verify $C_{\rm HH}$. The cycle was resumed till stopped [25]. Fig. 8 carries out that the annealing treatment seems to reduce substantially the localized state density.

Opposite to both strong accumulation and inversion voltage regions, along the depletion region a large frequency dependence has been observed for the measured admittance (Fig. 3a). In other words, under gate voltage modulation of frequency ω , the localized states within the BN film, more or less distant from the interface can exchange holes with the silicon valence band by Shockley-Read-Hall (SRH) statistics in two step mechanism [26]: first a hole is exchanged between the silicon valence band and the interface states near the silicon Fermi level and then in series, the interface state may exchange carriers with traps located inside the BN film at the distance x from the interface by tunnelling (tunneling probability of a carrier at the interface to reach the depth $x \propto \exp(-Kx)$ where $K^2 = 2 m U/\hbar^2$ with U is the effective potential depth of the trap to the relevant band edge [11]). For a given couple of frequency (ω) and temperature (*T*), there exits a position x_t such that for $x < x_t$ the charge of all states can follow the voltage modulation, for $x > x_t$ the opposite occurs and for boundary position $x = x_t$ the states can only partially answer the modulation with the following condition:

$$\omega \tau_{\rm t} = 1 \tag{14}$$

where $\tau_t = (e_p + c_p p_s)^{-1} = \text{emission time determined by SRH statistics with } e_p = \text{emission rate, } c_p = \text{capture coefficient} = \sigma_{px}v_{th}$ with $\sigma_{px} = \sigma_p \exp(-Kx) = \text{reduced capture cross section of the trap viewed by a carrier at the interface, <math>\sigma_p = \text{capture cross section of the trap located in the film at a distance x from the interface, <math>v_{th}$ = thermal velocity of the free holes, $p_s = p_0 \exp(-q\psi_s/kT)$ = free hole concentration at the interface, p_0 = free hole concentration in the bulk of Si.

If Fermi-Dirac distribution holds, $e_p = c_p p_s$ the relation (14) leads to:

$$Kx_{t} + \frac{q\psi_{s}}{kT} = \ln\left(\frac{\text{const.}}{\omega}\right)$$
(15)

On the other hand, the effective density of interface state D_{it} may be expressed as:

$$D_{\rm it} = N_{\rm t} x_{\rm t} \tag{16}$$

where N_t = number of localized trap per unit volume per unit energy interval in the BN film. The relation (15) explains the strong frequency dependence of the capacitance along the depletion region; for a given V_G (so a constant ψ_s):

- at higher frequency, the charge modulation on the gate electrode is counterbalanced by the charge modulation at the depletion edge since $x_t \approx 0$ and then $D_{it} \approx 0$, leading to:

$$C_{\rm m} \approx \frac{C_{\rm BN}C_{\rm D}}{C_{\rm BN}+C_{\rm D}}$$
 with $C_{\rm D} =$ depletion capacitance (17)

- at lower frequency, x_t is larger, and hence D_{it} is dominant and

$$C_{\rm m} \approx C_{\rm BN}$$
 (18)

- at intermediate frequency, the weighted average of D_{it} and depletion modulation is effective for defining the measured capacitance:

$$\frac{C_{\rm BN}C_{\rm D}}{C_{\rm BN}+C_{\rm D}} < C_{\rm m} < C_{\rm BN} \tag{19}$$

The physical origin of the measured D_{it} at the interface around the midgap of the BN film may be associated with the dangling bonds (DB) of both boron and nitrogen atoms. Considering boron rich nature of BN film at hand (determined by XPS analysis [22]), boron dangling bonds, (BN)_B should be dominant; but this seems in contradiction with the measured optical gap (\approx 5.2 eV) [13] indicating a rather stoichiometric hexagonal BN film. This inconsistency may be eliminated by taking into account the contamination of oxygen detected by IR spectroscopy (Fig. 2); these oxygen atoms, replacing rather nitrogen site would enlarge the optical gap since it is more electronegative than the nitrogen atom. Consequently boron abundance and oxygen contamination seem to have competing effects leading apparently to a gap value of stoichiometric film.

The increase of Urbach energy (E_0) by annealing may be explained by the increase of bond angle and bond length stresses due to the dehydrogenation effect of annealing; these stresses would increase the tail state density corresponding to a larger Urbach energy (E_0) .

However, on the contrary of the tail state density, the deep state density should decrease due to the improvement of nitrogen deficiency during the annealing treatment under nitrogen atmosphere. As a result, with respect to the localized density of states, the annealing may have opposite effects in the sense that the tail state density is enhanced while the deep state density is reduced by partially restoring the nitrogen deficiency and saturating boron dangling bonds.

Although D_{it} is drastically reduced by an annealing of 475 °C under N₂ flow (Fig. 4), a further reduction of D_{it} has not been observed for an annealing of 650 °C N₂ atmosphere; on the contrary, a slight increase is discernible. This might be interpreted as follows: the dehydrogenation, by reducing the density of saturated B—H and N—H bonds, may increase the density of deep states due to the dangling bonds, depicted in Fig. 7; in addition, the relaxing hydrogen in the BN film continues to be evolved when annealing temperature increases, leaving behind a more stressed structure, and hence

in this strained structure, the dangling bond density is reasonably expected to be increased. Unfortunately, the reduction of the localized density of deep states to an acceptable amount seems avoided by an accompanying structural change.

The difference between the D_{it} distributions obtained by both continuum and statistical models remains within the experimental error for 'as-grown' and 475 °C annealed samples which might be attributed to a relatively homogeneously distributed traps throughout the interface plane. This result seems in agreement with the existence of an interfacial BN amorphous layer of 2–3 nm thick containing the majority of traps measured by the ac conductance methods. However, a slight difference existing between the D_{it} distributions obtained by continuum and statistical models for 650 °C annealing carries out that a partial turbostratic crystallization of the amorphous interfacial layer occurs and then an inhomogeneous trap distribution in such turbostratic BN film is expected leading to the measured statistical distribution of D_{it} .

5. Conclusion

Optical testings of plasma deposited BN thin film pointed out an oxygen contaminated turbostratic structure (more or less parallel and disoriented hexagonal crystallites of distributed sizes were embedded in a disordered phase). A complete admittance analysis of BN film through an MIS (Al/BN film/Si) structure was attempted for the first time. A very large amount of D_{it} was measured. The effects of annealing treatments on the D_{it} were assessed and interpreted by assuming an amorphous interfacial layer of 2–3 nm thickness. Finally, for the first time, a detailed speculation about eventual origins of electronic defects was proposed.

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