Characterization of deep acceptor level in as-grown ZnO thin film by molecular beam epitaxy*

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We report deep level transient spectroscopy results from ZnO layers grown on silicon by molecular beam epitaxy (MBE). The hot probe measurements reveal mixed conductivity in the as-grown ZnO layers, and the current–voltage (I–V) measurements demonstrate a good quality p-type Schottky device. A new deep acceptor level is observed in the ZnO layer having activation energy of 0.49 ± 0.03 eV and capture cross-section of 8.57×10^{-18} cm^2. Based on the results from Raman spectroscopy, photoluminescence, and secondary ion mass spectroscopy (SIMS) of the ZnO layer, the observed acceptor trap level is tentatively attributed to a nitrogen–zinc vacancy complex in ZnO.

Keywords: ZnO, secondary ion mass spectroscopy, photoluminescence, Raman spectroscopy

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1. Introduction

ZnO is a very promising material for short-wavelength electronic and optoelectronic devices due to its large band gap (3.37 eV) and high exciton binding energy (60 meV) at room temperature.[1,2] Due to these desirable properties, ZnO is a candidate material for use in ultraviolet (UV) light emitting diodes, laser diodes, UV photo detectors, and solar cells.[3–5] ZnO is intrinsically an n-type material, and p-type doping is difficult to achieve due to the compensating behavior of the intrinsic donors.[6] Notwithstanding, we can find several reports on p-type conductivity of ZnO, however stable and reproducible p-type ZnO is still a challenge.[7–9] The possible reasons may include the low solubility of acceptors, the compensating effects of donors, and the deep level behavior of p-type dopants. Nitrogen is considered the best p-type dopant in ZnO, however the mechanism for the p-type conductivity associated with N is still a puzzle and under debate, because different activation sites of N have been reported in the band gap of ZnO. The most familiar ones are nitrogen on the O site (N_O), nitrogen on the Zn site (N_{Zn}), N_O–V_{Zn}, V_{Zn}–N_O–H^+, and the cluster of four nitrogen atoms around Zn. The chances of N_O and N_{Zn} to act as the hole conductivity sources are minimal due to their exceptionally deep energy states (1.31 eV and 1.71 eV, respectively)[10,11] in the band gap of ZnO. However, Park *et al.*[12] and Li *et al.*,[13] using the local density approximation (LDA) method, reported N_O at lower energy levels of 0.40 eV and 0.31 eV, respectively. On the other hand, the N_O–V_{Zn} complex with energy level 0.40 eV above the valence band maximum has been attributed (theoretically) to the double donor metastable state of N_{Zn}–V_O.[14] A similar explanation has been given by Reynolds *et al.*[15] for the H^- induced transformation of the N–V_{Zn} donor complex into V_{Zn}–N_O–H^+ as the acceptor level at 0.13 eV, while Reshchikov *et al.*[16] found experimentally an acceptor state in molecular beam epitaxy (MBE) grown N:ZnO at 0.40 eV and attributed it to the V_{Zn} complex. Recently, Muret *et al.*[17] reported a hole trap (HT5) with activation energy 0.48 eV and capture cross-section 4.7×10^{-14} cm^2 using deep-level transient spectroscopy (DLTS). They demonstrated that the defect was due to the involvement of nitrogen, however the real origin was not explained in their work. An overview of the current proposed acceptor defect levels in ZnO and their possible origin can be found in Table 1. It can be seen that various nitrogen centers are scattered within the band gap of ZnO and their origin is far from being clear. Therefore the characterization of the acceptor level states in ZnO is of interest and still needs further investigation.

In this paper, we report a new hole (acceptor) trap having activation energy 0.49 ± 0.03 eV above the valence band in MBE-grown ZnO on Si determined by DLTS. With the results of Raman scattering, photoluminescence, and secondary ion mass spectroscopy (SIMS) of the ZnO layer, the observed acceptor trap level is tentatively attributed to the nitrogen–zinc vacancy complex in ZnO. The experimental observation is compared with the available data in the literature.

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Table 1. Reported activation energy levels and origin of acceptor levels in the nitrogen-doped ZnO.

$E_v + E_t$/eV	σ/cm^2	Growth technique	Characterization method	Origin	Ref.
0.48	4.7×10^{-14}	MBE	experimentally: DLTS	N-related defect	[17]
0.19	3.0×10^{-15}	MBE	experimentally: DLTS	N-related defect	[17]
0.40	–	MBE	PL	V_{Zn} related complex	[16]
1.70	–	SCV	PL	N_O	[11]
0.13	–	OMVPE	PL	V_{Zn}–N_O–H^+	[15]
1.30	–	–	DFT	N_O	[10]
0.40	–	–	DFT-LDA	N_O–V_{Zn}	[14]
0.40	–	–	DFT-LDA	N_O	[12]
0.31	–	–	DFT-LDA	N_O	[13]
0.49	8.6×10^{-18}	MBE	experimentally: DLTS, PL, Raman, SIMS	N–V_{Zn}	this study

2. Experiment

ZnO layers were grown on a 3-inch diameter p-type silicon (001) wafer ($N_A \sim 1.2 \times 10^{15}$ cm^{-3}) by MBE. The ZnO was grown under the following conditions. The substrate temperature was set at 430 °C, oxygen was supplied from a radio-frequency (RF) atomic source, and Zn was evaporated from a Zn-Knudsen cell maintained at 289 °C filled with Zn beads of purity 99.9999%. The pressure of the chamber during the growth was $\sim 1 \times 10^{-4}$ mbar mainly due to the pressure required to operate the oxygen RF atomic source, and the growth time was 7 h. The oxygen RF atomic source was operated at 300 W. The thickness of the as-grown ZnO with respect to the clean part of the Si wafer used for the ZnO growth was found to be 500 ± 50 nm with the help of a step profilometer (the thickness value was confirmed in the SIMS measurement). Energy dispersive X-ray measurements revealed that the as-grown ZnO layer was O-rich. The observation was confirmed by secondary ion mass spectroscopy, yielding Zn:O $\sim 10^{19}$ atoms·cm^{-3}: 10^{18} atoms·cm^{-3} down to depth 500 nm of the layer. The SIMS data also demonstrated nitrogen traces with a concentration of 10^{16} atoms·cm^{-3} in the grown layers. The hot probe measurement on various parts of the as-grown ZnO layer clearly indicated the p-type conductivity of the layer: p-ZnO/p-Si. For electrical measurements, gold Schottky contacts with area 78 mm^2 were fabricated by electron beam evaporation. For comparison, similar contacts were also prepared on the clean part of the p-Si wafer. The characterization of the ZnO films was carried out by using the following methods (equipment manufacturer): DLTS (DLS-83D Hungry), SIMS (Cameca IMS 5f), and photoluminescence, and Raman spectroscopy (Mini PL-Raman spectrometer by Photonics).

3. Results and discussion

3.1. Transport measurements

The current–voltage (I–V) measurements were performed at 300 K for the Au/ZnO/Si Schottky diode, and the results are shown in Fig. 1. The ideality factor and the barrier height are calculated using the thermionic emission model with equations[18]

$$n = \frac{q}{kT \times s}, \tag{1}$$

$$\varphi_{B(I-v)} = \frac{kT}{q} \ln\left(\frac{AA^*T^2}{I_s}\right), \tag{2}$$

where q is the charge (C), k is the Boltzmann constant (J/K), T is the temperature (K), s is the slope of the forward-biased semilogarithm I–V curve, A is the Schottky contact area (cm^2), A^* is the Richardson constant (J/cm^2·K), and I_s is the reverse saturation current (A). The ideality factor is determined from the slope of the forward-biased semilogarithm I–V curve (Fig. 1). The calculated ideality factor is 3.20 at 300 K, which is higher than the reported values in the literature for gold Schottky contacts.[19] The higher ideality factor can be attributed to the interfacial thin insulator layer at the Au and ZnO interface, the series resistance effect, and the bias dependence of the barrier height (the presence of the interfacial thin insulator layer also supports the p-type conductivity signal of ZnO without a contribution from the p-Si substrate). The measured barrier height is found to be 0.70 eV, which is similar to that typically reported in the literature: the calculated barrier heights of Pd, Ag, Au Schottky diodes varied from 0.6 eV to 0.8 eV.[20] Therefore, this value seems to be reasonable. The acceptor concentration is calculated using the standard formula with the slope of the V–$(A/C)^2$ plot (not shown here)

$$N_d = \frac{-2}{q\varepsilon_0\varepsilon_r \mathrm{d}(A/C)^2/(\mathrm{d}V)}, \tag{3}$$

where q (1.6×10^{-19} C) is the charge of an electron, ε_0 (8.85×10^{-14}) is the permittivity of the free space, ε_r (9.66) is the relative permittivity of the medium, A is the area of the Schottky contact (78 mm^2), and C is the capacitance in units of pF. The calculated doping concentration is $\sim 8.0 \times 10^{16}$ cm^{-3}.

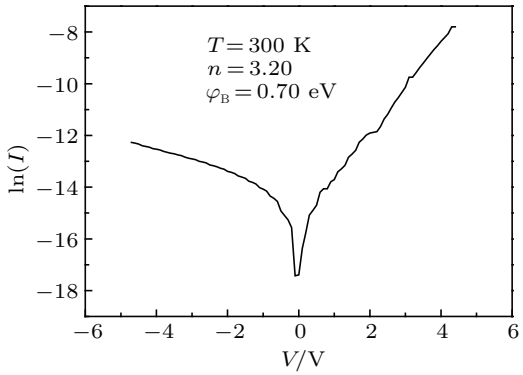


Fig. 1. Room temperature *I*–*V* measurements of the Au/ZnO/Si Schottky diode, the ideality factor and the barrier height at room temperature are calculated to be 3.20 and 0.70 eV, respectively.

3.2. DLTS measurements

DLTS is the most powerful and standard electrical technique that provides quantitative information about the deep energy level position, capture cross-section, and trap concentration.[21] Figure 2 displays a typical DLTS spectrum of an as-grown MBE ZnO layer measured under the following conditions: reverse bias $U_R = -1$ V, filling pulse $V_p = 0$ V, and filling time $t_p = 20$ s. The lock-in frequency of 1500 Hz (3255 s^{-1}) and the biasing conditions are deliberately chosen to avoid any contribution from the Si substrate. One acceptor (hole) trap is observed at temperature 357 K and referred to as H1. The activation energy and the trap capture cross-section (trap concentration) determined from the Arrhenius plot shown in Fig. 3 are $E_V + 0.49 \pm 0.03$ eV and 8.57×10^{-18} cm^2, respectively. The inset of Fig. 2 shows the DLTS spectrum from the clean part of the same wafer, the spectrum is clean, which hence confirms that the H1 level comes from the ZnO layer.

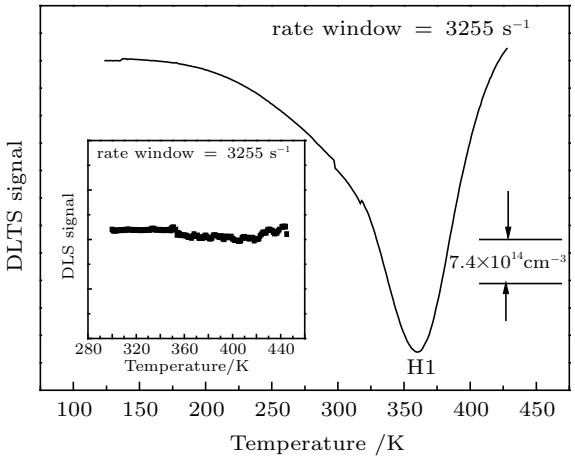


Fig. 2. Typical DLTS spectrum of the ZnO thin film grown on Si substrate at 1500 Hz (rate window 3255 s^{-1}). Inset shows the DLTS spectrum of Si at 1500 Hz under the same measuring conditions (lock-in principle).

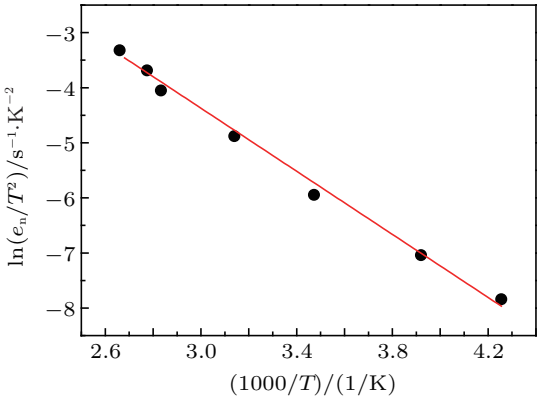


Fig. 3. (color online) Representative emission rate signatures (Arrhenius plot) of deep acceptor level H1 in the MBE grown ZnO on Si substrate.

The emission rate signatures together with the capture cross-section of the defect and the SIMS results suggest that the defect is associated with the N–Zn vacancy complex. It has been reported that in O-rich ZnO, Zn vacancies might have a lower formation energy, therefore a high density of Zn vacancies in our O-rich ZnO is reasonable.[22] It is also demonstrated in the literature that N can form different energy levels in the whole band gap of ZnO.[17] We argue that at least one of the nitrogen defect levels in ZnO exhibits a metastable behavior and cannot be stable. This metastable N atom may form a complex with the Zn vacancy and appears at 0.49 eV above the valence band maximum. A hole defect with activation energy 0.48 eV and capture cross-section 4.7×10^{-14} cm^2 was recently reported by Muret *et al.*[17] using DLTS, and they called it the N-related defects. Compared to the data of Muret *et al.*, the much lower capture cross-section (8.57×10^{-18} cm^2) exhibited by the H1 level in our sample gives a strong justification that the Zn vacancy and/or di-vacancy might be involved with the N ion. We also performed some additional measurements to support our argument.

3.3. SIMS analysis

Figure 4 shows the depth profiles of oxygen, zinc, and nitrogen revealed from the SIMS measurement. The nitrogen atoms have diffused throughout the 0.5 μm ZnO layer (the thickness of the as-grown ZnO layer), and have almost a constant concentration in the film. Its concentration is appreciably reduced at the interface between the ZnO film and the Si substrate. The atomic concentrations of O, Zn, and N calculated from the SIMS data are $\sim 1.3 \times 10^{18}$ atoms/cm^3, 1.2×10^{18} atoms/cm^3, and 1×10^{16} atoms/cm^3, respectively, therefore we believe that the prepared sample is ZnO. The X-ray diffraction (not shown in this manuscript) and photoluminescence measurements also confirmed that the prepared sample is ZnO with a hexagonal structure. The concentrations of Zn, O, and N were calculated after calibration using a standard sample. The reduction of the Zn content in the ZnO layer

is probably due to the nitrogen interplay during the growth. Whilst the source of the introduction of nitrogen into the MBE reactor is not clear, the involvement of nitrogen in oxygen gas flow allowed into the MBE chamber and/or a relatively high base pressure ($\sim 10^{-6}$ Torr) cannot be avoided.

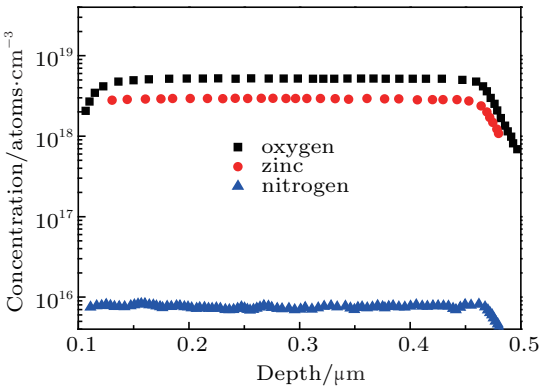


Fig. 4. (color online) SIMS data of the ZnO thin film grown on Si substrate by MBE, demonstrating the concentrations of O, Zn and N to be $\sim 10^{18}$ cm^{-3}, 10^{17} cm^{-3}, and 10^{16} cm^{-3}, respectively.

3.4. Photoluminescence

Figure 5 shows the room temperature photoluminescence (PL) spectrum of ZnO grown by MBE. The spectrum consists of two peaks at 2.2 eV and 3.28 eV. We relate these two peaks to the defect emission and the near band gap emission, respectively. The inset of Fig. 5 shows the defect emission PL peak of ZnO. We argue that the defect emission peak at 2.2 eV is related to the V_{Zn}–N defect complex. Reshchikov *et al.*[16] demonstrated the origin of this peak in N-doped ZnO layers grown by MBE as the defect complex that may include a Zn vacancy having activation energy 0.4 eV above the valence band. The activation energy of the reported defect complex was indirectly extracted from the 2.2 eV thermal shift of the YL band in the PL spectrum as function of the temperature of the sample, we believe that that technique could not be as accurate as DLTS, therefore the attribution of H1 with the N–Zn vacancy is more likely.

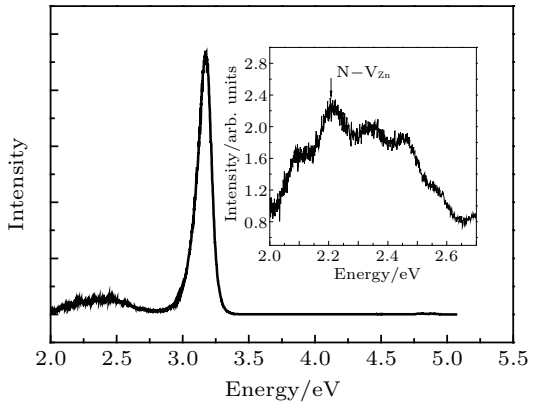


Fig. 5. Room temperature PL spectrum of the MBE grown ZnO consisting of near band emission and defect peaks. The inset shows a peak at 2.2 eV, which is related to the N–Zn vacancy complex.

3.5. Raman spectroscopy

Raman spectroscopy of the layer is displayed in Fig. 6, which confirms the O-rich status of ZnO, as the intensity of E_2^{high} is higher than that of A_1(LO) modes appearing at 437 cm^{-1} and 577 cm^{-1}.[23] Based on the previous reports, the peaks at 643 cm^{-1} and 850 cm^{-1} in Fig. 6 are attributed to the nitrogen-related defects.[24–26] Wu *et al.*[25] and Friedrich *et al.*[26] suggested that the vibrational mode at 275 cm^{-1} originates from the Zn interstitials where parts of their nearest neighbor O atoms are replaced by N atoms to form Zn_i–N_O. Obviously, this peak is absent in our O-rich samples. So the presence of higher-wavenumber Raman peaks (643 cm^{-1} and 850 cm^{-1} in Fig. 6) strongly supports the connection of N–Zn vacancy type defects in ZnO. The other peaks at 300 cm^{-1} and 512 cm^{-1} are related to the silicon substrate.[27,28] Relying on the Raman data, we understand that our sample has Zn vacancies and nitrogen-related structural defects, henceforth, our argument relating the origin of the H1 level to the N–V_{Zn} complex is more likely.

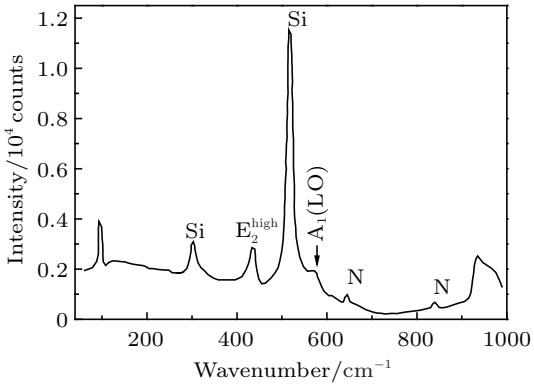


Fig. 6. Raman spectrum of the MBE grown ZnO on Si substrate. The higher intensity of the E_2^{high} mode as compared to the A_1(LO) mode demonstrates the O-rich status of the sample.

4. Conclusion

In conclusion, we have used the deep level transient spectroscopy to show a new hole trap in the as-grown ZnO prepared by molecular beam epitaxy. Based on the growth conditions, experimental evidence of nitrogen in the sample, and the results from the associated diagnostic techniques applied to the samples, we attributed the H1 ($E_V + 0.49$) deep level defect to the N–V_{Zn} complex in the ZnO lattice. The SIMS results confirmed the presence of nitrogen and the oxygen rich growth of the layers. The PL measurements also verified the presence of Zn-vacancy-related complex with photo energy 2.2 eV. The presence of higher-wavenumber Raman peaks (643 cm^{-1} and 850 cm^{-1}) strongly supported the connection of N–Zn vacancy type defects in ZnO. We boldly conclude that while nitrogen being involved with the intrinsic vacancy defects forms a deep acceptor complex in ZnO and therefore may not contribute to the p-type conductivity of ZnO.

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References

[1] Qiang M, Teguh Endah S, Akihisa O and Masaaki N 2011 *Appl. Phys. Lett.* **98** 051908
[2] Muhammad A, Khalid M, Ian F, Yasin A Raja, Ya-Hong X, Raphale T and M-Ali H 2013 *Semicond. Sci. Technol.* **28** 105019
[3] Wang L M, Chiam S Y, Huang J Q, Wang S J, Pan J S and Chim W K 2011 *Appl. Phys. Lett.* **98** 022106
[4] Sang Wuk L, Hak Dong C, Gennady P and Won T 2011 *Appl. Phys. Lett.* **98** 093110
[5] Sushant G, Purushottam K, Arul C A, Doina C and Singh R K 2011 *Appl. Surf. Sci.* **257** 5837
[6] Ying C and Fabien B 2010 *Appl. Phys. Lett.* **97** 042108
[7] Dongqi Y, Lizhong H, Shuangshuang Q, Heqiu Z, Song-En Andy L, Len L K, Qiang F, Xi C and Kaitong S 2009 *J. Phys. D: Appl. Phys.* **42** 055110
[8] Pan X H, Jiang J, Zeng Y J, He H P, Zhu L P, Ye Z Z, Zhao B H and Pan X Q 2008 *J. Appl. Phys.* **103** 023708
[9] Qin J M, Yao B, Yan Y, Zhang J Y, Jia X P, Zhang Z Z, Li B H, Shan C X and Shen D Z 2009 *Appl. Phys. Lett.* **95** 022101
[10] Lyons J L, Anderson J and Cress V W 2009 *Appl. Phys. Lett.* **95** 252105
[11] Tarun M C, Zafar I and McCluskey M D 2011 *AIP Advances* **1** 022105
[12] Park C H, Zhang S B and Wei S H 2002 *Phys. Rev. B* **66** 073202
[13] Jiangbo L, Su-Huai W, Su-Shen L and Jian-Bi X 2006 *Phys. Rev. B* **74** 081201
[14] Lei L, Jilian X, Dandan W, Mingming J, Shuangpeng W, Binghui L, Zhenzhong Z, Dongxu Z, Chong-Xin S, Bin Y and Shen D Z 2012 *Phys. Rev. Lett.* **108** 215501
[15] Reynolds J G, Reynolds C L, Mohanta Jr. A, Muth J F, Rowe J E, Everitt H O and Aspnes D E 2013 *Appl. Phys. Lett.* **102** 152114
[16] Reshchikov M A, Xie J Q, Hertog B and Osinsky A 2008 *J. Appl. Phys.* **103** 103514
[17] Pierre M, Dimitri T, Christian M and Jean-Michel C 2012 *Appl. Phys. Lett.* **101** 122104
[18] Sadia F, Hadia N, Muhammad A, Willander M and Qamur W 2009 *Adv. Mater. Research* **79-82** 1317
[19] Aydogan S, Cinar K, Asıl C H, Kun C C and Türüt A 2009 *J. Alloy. Comp.* **476** 913
[20] Auret F D, Goodman S A, Hayes M, Legodi M J, Van Laarhoven H A and Look D C 2001 *Appl. Phys. Lett.* **79** 3074
[21] Lang D V 1974 *J. Appl. Phys.* **45** 3014
[22] Fumiyasu O, Minseok C, Atsushi T and Isao T 2011 *Sci. Technol. Adv. Mater.* **12** 034302
[23] Soumen D and Giri P K 2012 *Thin Solid Films* **520** 5000
[24] Kennedy J, Carder D A, Markwitz A and Reeves R J 2010 *J. Appl. Phys.* **107** 103518
[25] Ke Yue W, Qing Qing F, Wei Na W, Chang Z, Wen Juan H, Jin Guang L, Qing Rong L, Yan Mei L, Qi Ping Z and Hang Ming Z 2010 *J. Appl. Phys.* **108** 063530
[26] Felic F, Gluba M A and Nickel N H 2009 *Appl. Phys. Lett.* **95** 141903
[27] Changzheng W, Zhong C, Haiquan H and Dong Z 2009 *Physica B* **404** 4075
[28] Muhammad A, Khalid M, Adnan A, M-Ali H, Yasin A R, Ijaz H and Willander M 2011 *ECS Trans.* **35** 149