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Formation and dissociation of hydrogen-related defect centers in Mg-doped GaN

O. Gelhausen[1], M. R. Phillips[1],E. M. Goldys[2], T. Paskova[3], B. Monemar[3], M. Strassburg[4,5] and A. Hoffmann[4]
[1]Microstructural Analysis Unit, University of Technology, Sydney, Broadway, NSW 2007 Australia
[2]Division of Information and Communication Sciences, Macquarie University, North Ryde, NSW 2109, Australia
[3]Material Science Division, Department of Physics and Measurement Technology, Linköping University, S-581 83 Linköping, Sweden
[4]Institute for Solid-State-Physics, Technical University Berlin, 10623 Berlin, Germany
[5]Department of Physics and Astronomy, Georgia State University, Atlanta, GA-30303, USA

ABSTRACT

Moderately and heavily Mg-doped GaN were studied by a combination of post-growth annealing processes and electron beam irradiation techniques during cathodoluminescence (CL) to elucidate the chemical origin of the recombination centers responsible for the main optical emission lines. The shallow donor at 20-30 meV below the conduction band, which is involved in the donor-acceptor-pair (DAP) emission at 3.27 eV, was attributed to a hydrogen-related center, presumably a (V_N-H) complex. Due to the small dissociation energy (<2 eV) of the (V_N-H) complex, this emission line was strongly reduced by low-energy electron irradiation. CL investigations of the DAP at a similar energetic position in Si-doped (n-type) GaN indicated that this emission line is of different chemical origin than the 3.27 eV DAP in Mg-doped GaN. A slightly deeper DAP emission centered at 3.14 eV was observed following low-energy electron irradiation, indicating the appearance of an additional donor level with a binding energy of 100-200 meV, which was tentatively attributed to a V_N-related center. The blue band (2.8-3.0 eV) in heavily Mg-doped GaN was found to consist of at least two different deep donor levels at 350±30 meV and 440±40 meV. The donor level at 350±30 meV was strongly affected by electron irradiation and attributed to a H-related defect.

INTRODUCTION

Low p-type carrier density even in state-of-the-art GaN has remains one of the biggest issues in GaN-based research. Currently, the level of p-type conductivity is good enough for light emitting diodes and just sufficient for laser diodes, but is inadequate for the fabrication of high-performance heterojunction bipolar transistors or GaN-based dilute magnetic semi-conductor (DMS) materials. In addition, the nature of dopants, defects and residual impurities and their impact on the p-type carrier concentration is not completely understood.

In this study, a comprehensive analysis of the luminescent emission properties of moderately and heavily Mg-doped GaN is carried out by combining post-growth annealing processes [1] and low-energy electron beam irradiation (LEEBI) techniques [2] as well as temperature- and excitation density-resolved CL spectroscopy. The combination of these techniques [3] represents a powerful approach to both investigate the optical properties and facilitate an assignment of the optical emission peaks in GaN to specific radiative recombination centers.

EXPERIMENTAL DETAILS

The samples studied were grown by MOVPE on a GaN buffer layer and c-plane sapphire substrate. Three different sets of samples were studied in this work. The first set was 2 μm thick, thermally activated GaN:Mg with a Mg concentration in the low 10^{19}cm^{-3} and a hole concentration of 1.0*10^{17}/cm^{3}, as determined by Hall measurements, while the second set was 2 μm thick GaN:Si with an electron concentration of 1.0-6.0*10^{18}/cm^{3}. These 2 sets were annealed in a gas-tight furnace in controlled atmospheres of high purity gases (N_2, O_2, H_2(5%)/N_2). The annealing protocol consisted of a 180s ramp from RT to 780°C, a plateau of 10 s and exponential cooling for 20 min. to RT. The third set, studied as-received, was 0.5 μm thick, semi-insulating GaN:Mg with a Mg concentration of in the 10^{20}cm^{-3} range. The CL measurements were carried out between 5 K and 300 K using an Oxford Instruments MonoCL2 system either installed on a JEOL35C or a LEO Supra 55VP SEM. The CL spectra were measured using a 1200 lines/mm grating blazed at 500 nm and a Hamamatsu R943-02 Peltier cooled PMT. All CL spectra were corrected for system response. The electron beam current, I_b, was measured using a Faraday cup.

RESULTS AND DISCUSSION

The two main compensation mechanisms in Mg-doped GaN are (i) passivation of Mg acceptors with donor-like H atoms [2] and (ii) self-compensation by point defects due to high Mg-doping [4]. In the moderate doping regime, 3 x 10^{18} cm^{-3} $\leq N_A \leq$ 2 x 10^{19} cm^{-3}, H passivation is very effective and impurity compensation as well as self-compensation mechanisms are negligible [4]. The effect of a doping-driven compensation becomes significant when the Mg concentration exceeds a value of $N_A \geq$ 2 x 10^{19}cm^{-3}. [4] PL results indicated that strong Mg doping of GaN generates three deep donor levels in addition to the shallow Mg acceptor, giving rise to a compensation mechanism that is directly related to the incorporation of Mg. [5] The CL emission of moderately Mg-doped GaN is dominated by a shallow donor-acceptor pair (DAP) emission at an energy of 3.25-3.28 eV [6,7] at low temperatures (Fig. 1). The chemical origin of this emission line is still under debate, since a similar line is sometimes observed in nominally undoped or Si-doped GaN as well (Fig. 2). However, there is a limited number of possible candidates both for the shallow acceptor and the shallow donor(s) involved in the DAP. For the shallow acceptor with an optical binding energy of around 225 meV, Mg_{Ga} [8,9] is the most promising candidate. Whereas possible candidates for the shallow donor (20-30 meV) are O [10], Si [11], H [12] and V_N-H [13].

To elucidate the chemical origin of this emission line, several samples from a Mg-doped (p-type) and a Si-doped (n-type) GaN wafer were annealed in three different atmospheres (N_2, O_2 and H_2(5%)/N_2) and subsequently investigated by CL spectroscopy. In Fig. 1, the 80 K CL spectra for three annealed and one untreated Mg-doped GaN samples are shown. The dominant 3.27 eV DAP emission line in the reference sample is strongly decreased after annealing in O_2 or N_2, but slightly increased after annealing in H_2/N_2-atmosphere. The impact of electron irradiation on the 3.27 eV emission line was investigated by monitoring its CL intensity during constant LEEBI with a higher beam current (20 nA) as a function of time (inset, Fig. 1). While the 3.27 eV DAP emission of the Mg-doped GaN annealed in O_2 and N_2 was not beam-sensitive at all, in the untreated and the H_2/N_2-annealed sample it was found to be reduced by one order of magnitude during LEEBI. This exponential decrease of the intensity of the 3.27 eV emission during electron irradiation indicates that one or both partners of the original DAP are not available for this recombination process anymore. This effect was permanent, i.e. after beam blanking for one hour no changes in the CL intensity were observed.

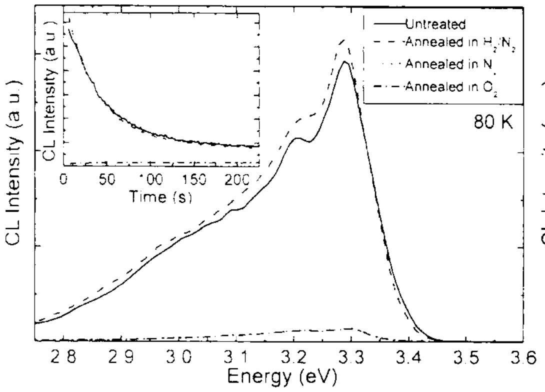

Figure 1. 80 K CL spectra [E_b=10 keV, I_b= 0.25 nA, 89μm x 71μm] of Mg-doped p-type GaN after post-growth annealing. The inset shows 80 K time-resolved CL measurements of the shallow DAP at 3.27 eV for untreated and annealed samples during LEEBI [E_b=10 keV, I_b=20 nA, 44μm x 35μm].

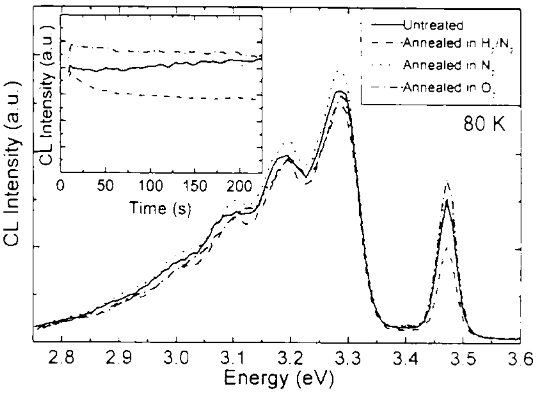

Figure 2. 80 K CL spectra of Si-doped n-type GaN after post-growth annealing under identical experimental conditions as in Fig.1. The inset shows 80 K time-resolved CL measurements of the shallow DAP at 3.27 eV for untreated and annealed samples during LEEBI [E_b=10 keV, I_b=20 nA, 44 μm x 35 μm].

A DAP emission line of similar energy is sometimes found in nominally undoped or Si-doped (n-type) GaN epilayers as well. Therefore, annealing and electron irradiation experiments were performed under identical conditions as in Fig. 1 for Si-doped GaN (Fig. 2). Annealing in both N_2, O_2 and H_2(5%)/N_2 did not affect the intensity of the 3.27 eV DAP emission line at all. Moreover, the effect of electron irradiation during CL is essentially negligible (Fig. 2, inset), which is a further indication that no beam-induced defects are generated under these conditions. Based on these observations, we conclude that the chemical origin of at least one partner of the DAP emission in Si-doped GaN is different from the DAP in Mg-doped (p-type) GaN.

In Mg-doped GaN, the shallow acceptor state is most likely Mg. In addition, Mg is a common contaminant in GaN. Recent SIMS data on HVPE GaN have confirmed this situation, showing that Mg is often present in HVPE GaN with concentrations in the 10^{16} cm^{-3} range [14]. The theoretical considerations in Ref. [15] suggest that it is highly unlikely that Mg is affected by the electron irradiation, which leads to the conclusion that the shallow donor, which needs to be identified, must be sensitive to electron exposure. Based on the presented annealing and electron irradiation results, O and Si can be ruled out as the donor in the 3.27 eV DAP emission. Si_{Ga} and O_N are believed to have a $E_{threshold}$ for the displacement of the Si (or O) atom of the same order of magnitude as that for Ga and therefore should not be affected by the electron beam [15]. Recently, H [12] and V_N-H [13] were proposed to be the shallow donor level in MOVPE-grown Mg-doped GaN. However, isolated H is expected to be a deep donor showing a negative U-behaviour [16]. Therefore, we tend to prefer the model by van de Walle [13], who predicted that the V_N-H complex is the shallow (double) donor responsible for the 3.27 eV emission in Mg-doped GaN and present in sufficient amounts under p-type conditions. Hence, both the electron irradiation and the annealing experiments are explained in terms of this model.

The time-dependence of the emission lines in moderately Mg-doped GaN was monitored during continuous electron exposure to elucidate what mechanisms cause the CL spectrum to decrease. At a beam energy of 2.5 keV (which corresponds to a primary electron penetration depth

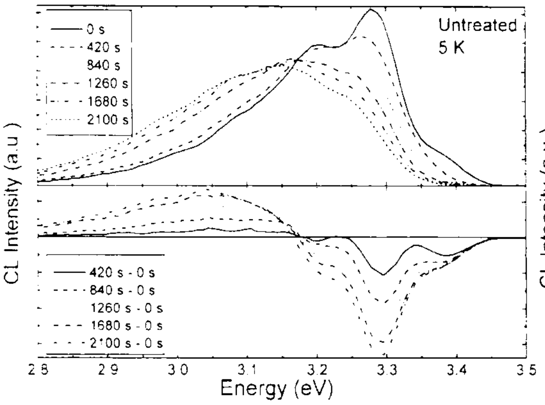

Figure 3. Upper part: 5 K CL spectra of Mg-doped p-type GaN taken repeatedly during LEEBI [E_b=2.5 keV, I_b=0.14 nA, 18 µm x 14 µm]. Time t=0 marks the end of the first spectrum. Lower part: Successive changes of the CL spectra, expressed as the difference between the first and the following spectra.

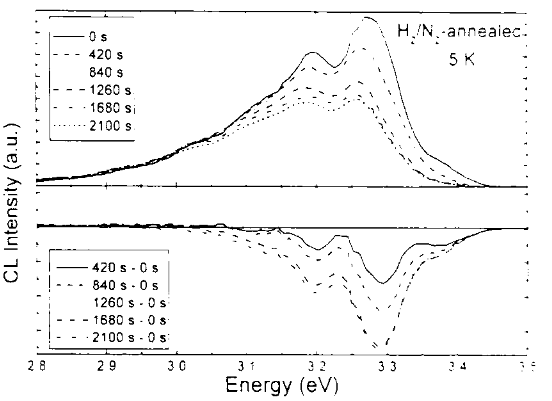

Figure 4. Upper part: 5 K CL spectra of Mg-doped p-type GaN (annealed in a H_2/N_2-atmosphere) taken repeatedly during LEEBI [E_b=2.5 keV, I_b=0.14 nA, probing area: 18 µm x 14 µm]. Lower part: Successive changes of the CL spectra, expressed as the difference between the first and the following spectra.

of ~50 nm [17]) three effects are observed (Fig. 3). First, the intensity of the 3.27 eV DAP decreased exponentially with irradiation time, second, a deeper emission band centered at around 3.05 eV (for an excitation density of E_b=2.5 keV and I_b=0.14 nA) emerged and third, the weak emission line, centered at approximately 3.37 eV and tentatively assigned to excitons deeply bound to centers located in structurally disturbed regions of GaN [18], is completely quenched as a result of the electron exposure. These effects are illustrated in the lower part of Fig. 3, where the differences of the first (original) and each of the following spectra are illustrated. These experiments were undertaken for a range of electron beam powers from E_b=2.5 keV and I_b=0.14 nA to E_b=30 keV and I_b=0.36 nA (not shown) and a gradual blueshift of the deeper emission line was observed, which saturated at 3.14 eV. This behaviour is characteristic for a DAP transition and represents a confirmation of other recent results [19]. Similar experiments were carried out for moderately Mg-doped (p-type) GaN annealed in H_2/N_2-atmosphere (Fig. 4). For the spectra taken during electron exposure at a beam energy of 2.5 keV, the 3.27 eV DAP and the 3.37 eV emission line decreased in the same way as in the reference sample (Fig. 3) but the deeper DAP between 3.05 and 3.14 eV was not observed. Therefore, it is reasonable to assume that the annealing in H_2/N_2 atmosphere prevents the formation or the activation of the 3.14 eV DAP recombination channel, which might indicate a decrease in the concentration of other compensating defects during H_2/N_2 anneal. The following model is proposed to account for the experimental results. The electron beam-induced dissociation of the V_N-H complexes generates isolated V_N and highly mobile H, which presumably complexes with other H or attaches to extended crystal defects. [20] Isolated V_N were found to have a binding energy of 64 ± 10 meV (according to temperature-dependent Hall data) or 180 meV (according to DLTS) [21] making V_N a possible candidate for the donor level in the 3.14 eV DAP. The time-dependent CL measure-ments of the samples annealed in H_2/N_2-atmosphere (Fig. 6) are then explained by a passivation or removal of V_N due to an excess amount of H during the annealing process, since it is energeti-cally more favourable to passivate the Mg acceptors by H than by intrinsic defects such as V_N [16].

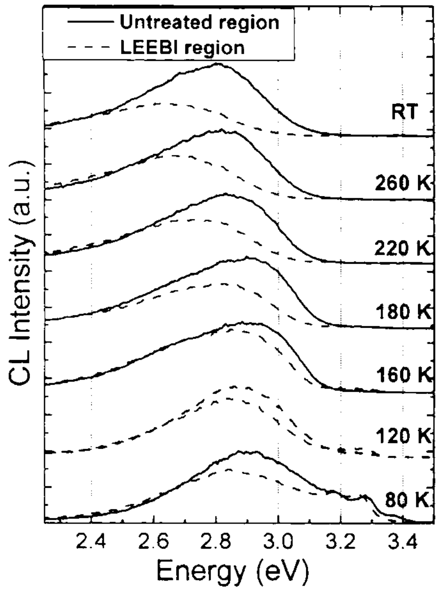

Figure 5. Norm. CL spectra at selected temperatures of an untreated and a LEEBI area, in compensated Mg-doped GaN (E_b=10 keV, I_b=0.3 nA, 24µm x 30µm). The LEEBI area was generated at 80 K using a beam power of 100 µW (E_b=10 keV, I_b=10 nA, 180 s).

In the high Mg-doping regime ($N_A \geq 2 \times 10^{19}cm^{-3}$) [4] a blue band centered at 2.8-3.0 eV forms (Fig. 5). The origin of this band is still not completely understood and recent experimental results indicate that it might consist of more than one emission band [5,22]. Most researchers agree that the blue band is caused by a transition between a deep localized donor and an acceptor state (likely a Mg-related acceptor) [4,5,23]. Both theoretical [4,24] and experimental [4,5] studies concluded that the incorporation of high Mg concentrations is accompanied by a formation of additional deep donors. The formation energy of these donors rapidly decreases as the Fermi-level approaches the valence band [13]. Likely candidates for deep donors in heavily Mg-doped GaN are V_N [13], Mg-V_N [4], V_N-H [12], Mg_i [22] and Mg_N [22]. To study the impact of electron irradiation on heavily Mg-doped (compensated) GaN, temperature-dependent CL spectra were collected both in untreated and LEEBI (10 kV, 10 nA, 180 s) areas of the sample (Fig. 5) From these experiments it is apparent that the blue emission band consists of at least 2 emission lines of different origin since the peak of higher energy (~2.95 eV at 80 K) is sensitive to electron exposure while the one at lower energy (~2.86 eV at 80 K) is not affected. The two donor levels are located at 350 ± 30 meV and 440 ± 40 meV below the conduction band. The level at 350 ± 30 meV is in excellent agreement with previous results [5]. With respect to the LEEBI results (Fig. 5), we postulate that this center is H-related since it exhibits a high sensitivity towards electron exposure. The level at 440 ± 40 meV is not affected by electron exposure and might be explained by Mg-V_N complexes, which are predicted to be the deep donors responsible for the self-compensation in heavily Mg-doped GaN and the observed blue band [4]. The thermal behaviour of these emission lines indicates that the electron irradiation-sensitive emission line is dominant at 300 K but less efficient at low temperature.

CONCLUSIONS

A combination of post-growth annealing processes and low-energy electron beam irradiation techniques during CL was used to determine the chemical origin of the main optical emission lines in moderately and heavily Mg-doped GaN. The 3.27 eV DAP emission line was found to be strongly affected by LEEBI. It is suggested that the acceptor in the 3.27 eV DAP emission is Mg and that the donor (20-30 meV) is hydrogen-related, presumably a V_N-H complex. This complex dissociated during electron irradiation and a deeper emission line (3.14 eV) emerged, which was assigned to a DAP consisting of the same Mg acceptor level and a deeper donor (100-200 meV). The blue band (2.8-3.0 eV) was found to consist of at least two different deep donor levels at 350±30 meV and 440±40 meV. The emission line related to the donor at 350±30 meV was reduced during electron irradiation and attributed to a H-related defect. Finally, a comparison of the UV DAP emission lines in Mg-doped (p-type) and Si-doped (n-type) GaN indicated that the respective recombination centers are of different chemical origin.

REFERENCES

1. S. Nakamura, N. Iwasa, M. Senoh, and T. Mukai, Jpn. J. Appl. Phys. **31**, 1258 (1992)
2. H. Amano, M. Kito, K. Hiramatsu, and I. Akasaki, Jpn. J. Appl. Phys. **28**, L2112 (1989)
3. O. Gelhausen, M. R. Phillips and E. M. Goldys, Journal of Physics D **36**, 2976(2003)
4. U. Kaufmann, P. Schlotter, H. Obloh, K. Köhler, and M. Maier, Phys. Rev. B **62**, 10867 (2000)
5. L. Eckey, U. von Gfug, J. Holst, A. Hoffmann, A. Kaschner, H. Siegle, C. Thomsen, B. Schineller, K. Heime, M. Heuken, O. Schön and R. Beccard, J. Appl. Phys. **84**, 5828 (1998)
6. W. Götz, N. M. Johnson, J. Walker, D. P. Bour and R. A. Street, Appl. Phys. Lett. **68**, 667 (1996)
7. A. Hoffmann, "Optical properties of GaN," in "Advances in Solid State Physics (Festkörperprobleme XXXVI)," (editor R. Helbig), ch. 2, 33–56, Vieweg & Sohn, Wiesbaden (1997)
8. I. Akasaki, H. Amano, M. Kito and K. Hiramatsu, J. of Luminescence **48 & 49**, 666 (1991)
9. E. R. Glaser, W. E. Carlos, G. C. B. Braga, J. A. Freitas, Jr., W. L. Moore, B. V. Shanabrook, R. L. Henry, A. E. Wickenden, D. D. Koleske, H. Obloh, P. Kozodoy, S. P. DenBaars and U. K. Mishra, Phys. Rev. B **65**, 853121 (2002)
10. C. Wetzel, T. Suski, J.W. Ager III, E.R. Weber, E.E. Haller, S. Fischer, B.K. Meyer, R.J. Molnar, P. Perlin, Phys. Rev. Lett. **78**, 3923 (1997)
11. W. Götz, N. M. Johnson, C. Chen, H. Liu, C. Kuo and W. Imler, Appl. Phys. Lett. **68**, 3144 (1996)
12. F. Shahedipour and B. W. Wessels, Appl. Phys. Lett. **76**, 3011 (2000)
13. C.G. van de Walle, Phys. Rev. B **56**, 10020 (1997)
14. B. Monemar, P. P. Paskov, T. Paskova, J. P. Bergman, G. Pozina, W. M. Chen, P. N. Hai, I. A. Buyanova, H. Amano and I. Akasaki, Mat. Science and Engineering B**93**, 112 (2002)
15. A. Ionascut-Nedelcescu, C. Carlone, A. Houdayer, H. J. von Bardeleben, J.-L. Cantin and S. Raymond, IEEE Transactions on Nuclear Science **49**, 2733 (2002)
16. J. Neugebauer and C. G. van de Walle, Phys. Rev. Lett. **75**, 4452 (1995)
17. P. Hovington, D. Drouin, and R. Gauvin, Scanning **19**, 1 (1997)
18. L. Eckey, J.-Ch. Holst, P. Maxim, R. Heitz, A. Hoffmann, I. Broser, B.K. Meyer, C. Wetzel, E. N. Mokhov P. G. Baranov, Appl. Phys. Lett. **68**, 415 (1996)
19. O. Gelhausen, H. N. Klein, M. R. Phillips and E. M. Goldys, Appl. Phys. Lett. **83**, 3293 (2003)
20. J. Neugebauer and C. G. van de Walle, Appl. Phys. Lett. **68**, 1829 (1996)
21. D. C. Look, D. C. Reynolds, Z.-Q. Fang, J. W. Hemsky, J. R. Sizelove and R. L. Jones, Materials Science and Engineering B **66**, 30 (1999)
22. M. Leroux, B. Beaumont, N. Grandjean, P. Lorenzini, S. Haffouz, P. Vennegues, J. Massies and P. Gilbart, Materials Science and Engineering B50, 97 (1997)
23. E. R. Glaser, W. E. Carlos, G. C. B. Braga, J. A. Freitas, Jr., W. L. Moore, B. V. Shanabrook, R. L. Henry, A. E. Wickenden, D. D. Koleske, H. Obloh, P. Kozodoy, S. P. DenBaars and U. K. Mishra, Phys. Rev. B **65**, 853121 (2002)
24. F. A. Reboredo and S. T. Pantelides, Phys. Rev. Lett. **82**, 1887 (1999)

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PREFACE

Symposium Y, "GaN and Related Alloys—2003," held December 1–5 at the 2003 MRS Fall Meeting in Boston, Massachusetts, was a continuation of a series of symposia that has been actively running for over a decade. The symposium was very well attended and indicated that the field is vibrant and growing rapidly. There were contributions from 28 different countries spanning 5 continents. The session topics included optical devices, bulk substrates, heteroepitaxy, nanostructures, material characterization, electronic devices, doping, theory, processing, and indium nitride. More than half of the 258 presented papers were submitted for inclusion in this proceedings volume. In addition to oral and poster presentations, the symposium also served as a forum for researchers to meet, exchange ideas, and form new collaborations.

There were many people involved in making this symposium a success. Special thanks are expressed to the session chairs, manuscript reviewers, symposium assistants, and authors of all invited and contributed papers. We are also grateful for the excellent support of the MRS staff who ensured that every organizational detail was addressed.

We would like to acknowledge the Air Force Office of Scientific Research (AFOSR), Army Research Office (ARO), Defense Advanced Research Projects Agency (DARPA), and Office of Naval Research (ONR) for their financial support of this symposium.

Hock Min Ng
Michael Wraback
Kazumasa Hiramatsu
Nicolas Grandjean

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