

Research Article

Vacuum Ultraviolet Field Emission Lamp Consisting of Neodymium Ion Doped Lutetium Fluoride Thin Film as Phosphor

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A vacuum ultraviolet (VUV) field emission lamp was developed by using a neodymium ion doped lutetium fluoride ($\text{Nd}^{3+} : \text{LuF}_3$) thin film as solid-state phosphor and carbon nanofiber field electron emitters. The thin film was synthesized by pulsed laser deposition and incorporated into the lamp. The cathodoluminescence spectra of the lamp showed multiple emission peaks at 180, 225, and 255 nm. These emission spectra were in good agreement with the spectra reported for the $\text{Nd}^{3+} : \text{LuF}_3$ crystal. Moreover, application of an acceleration voltage effectively increased the emission intensity. These results contribute to the performance enhancement of the lamp operating in the VUV region.

1. Introduction

Vacuum ultraviolet (VUV) light has been used in numerous fields, such as cleaning, surface modification, and sterilization, because short wavelength light with high photon energy is capable of breaking strong chemical bonds [1–3]. Therefore, performance improvements of VUV lamps contribute to the progress of these applications. The VUV gas lamp has widely been used [4–6] but presents limited stability, lifetime, and size. VUV lamps using a solid-state phosphor have attracted considerable attention as alternate light sources because they exhibit less deterioration, less fluctuation, and higher density than gas lamps [7, 8]. These lamps require wide band gap materials but few solid-state phosphors have substantial band gaps. Group III nitrides are suitable because they present a direct transition type band structure with a wide band gap

[9, 10]. However, even when using AlN, which emits light at a relatively short wavelength, the operating wavelength was limited to deep UV region [9, 11–13]. The wide band gap of diamond can be applied to UV but not to VUV lamps [14]. On the other hand, some fluorides have band gaps that are sufficiently wide to enable light emission in the VUV region [15, 16]. Fluoride composite materials have been widely studied as laser materials, scintillation materials, and optical materials because of their extremely wide band gap [17–24]. Specifically, a KMgF_3 thin film acting as a solid-state phosphor and carbon nanofiber (CNF) field electron emitter has previously been incorporated into a VUV lamp [25]. The emission spectra from the lamp showed two emission peaks at 155 and 180 nm in the 140–200 nm wavelength range, showing that solid-state phosphors can be exploited in VUV lamps.

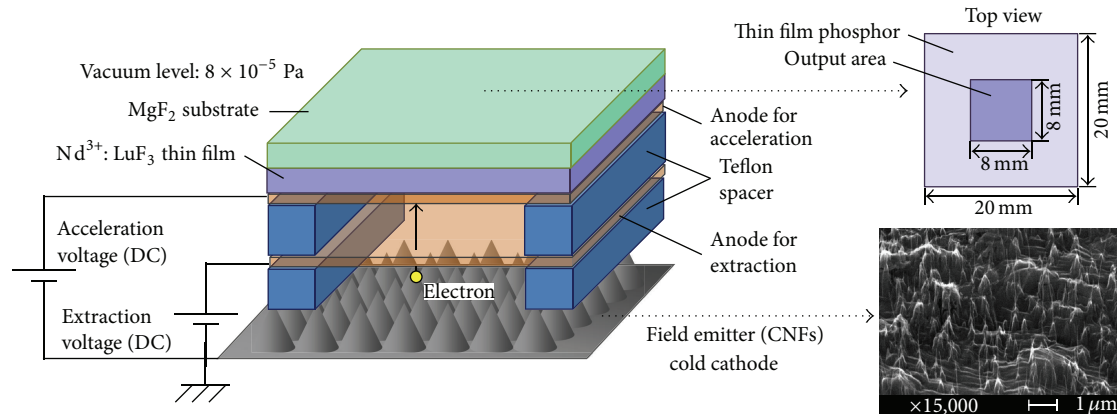


FIGURE 1: Schematic diagram of VUV field emission lamp. SEM image of CNFs is shown in the insert.

Neodymium ion doped lutetium fluoride ($\text{Nd}^{3+}:\text{LuF}_3$), whose cathodoluminescence (CL) efficiency is almost equivalent to KMgF_3 , was selected as a phosphor to develop a new VUV lamp. This lamp also consisted of CNFs field electron emitters. Among Nd^{3+} ion doped fluoride materials that emit VUV light, such as $\text{Nd}^{3+}:\text{LuF}_3$, $\text{Nd}^{3+}:\text{LaF}_3$, and $\text{Nd}^{3+}:\text{LuLiF}_4$ [26–28], $\text{Nd}^{3+}:\text{LuF}_3$ single crystals have reported the highest X-ray excited luminescence conversion efficiency [26]. However, large $\text{Nd}^{3+}:\text{LuF}_3$ single crystals have proven difficult to grow because of the occurrence of a hexagonal to orthorhombic phase transition (ca. 950°C) during the crystal growth process [26]. The stress caused by this structural reconfiguration results in crack formation in $\text{Nd}^{3+}:\text{LuF}_3$ single crystals. In contrast, growth of thin film suppresses these cracks owing to reducing stress by depositing small particles. For this reason, we fabricated $\text{Nd}^{3+}:\text{LuF}_3$ thin film by pulsed laser deposition (PLD) to deposit small particles. In addition, PLD has produced fewer chemical composition discrepancies between source targets and deposited thin films. Consequently, the fabrication of fluoride thin films by PLD does not require the utilization of the toxic fluorine gas [29].

2. Experimental Methods

2.1. Thin Film Fabrication. The target was prepared by pressing a 1:9 NdF_3 - LuF_3 powder mixture. A (001)-oriented MgF_2 crystal ($20\text{ mm} \times 20\text{ mm} \times 0.5\text{ mm}$) mounted on a rotating holder was used as a substrate and was maintained at 400°C during PLD. This substrate temperature was chosen because previous experiments on the growth of $\text{Nd}^{3+}:\text{LaF}_3$ thin films showed that substrate heating improved crystalline quality and VUV luminescence quantum efficiency and resulted in optimal performance at 400°C [27]. The thin film was deposited by irradiating the $\text{Nd}^{3+}:\text{LuF}_3$ target with the third harmonics of a Nd:YAG laser (355 nm in wavelength). The 2 mm diameter laser spot was focused on the target at a fluence of $2.5\text{ J}/\text{cm}^2$ and a repetition rate of 10 Hz. The deposition was carried out for 8 h at an average pressure of $3 \times 10^{-4}\text{ Pa}$ without atmosphere control.

2.2. Field Emission Lamp Construction. CNFs were grown by bombarding a grassy carbon substrate with Ar^+ at room temperature [30–32]. The ion beam, which had a diameter of 6 cm, was set at an incident angle of 45° and energy of 1 keV, respectively. The length and diameter of CNFs were 0.3–2 and 20 mm, respectively, with an approximate density of $5 \times 10^8\text{ cm}^{-2}$. Figure 1 shows the schematic of the lamp. In addition to the CNFs and the thin film, the lamp contained two copper mesh electrodes with a mesh width of 0.1 mm. Two teflon spacer plates were used to prevent short circuits and provide space for electron acceleration. A $200\text{ }\mu\text{m}$ thick spacer was placed between CNFs and a copper electrode and a 5 mm thick spacer was placed between the two copper electrodes. In this lamp, electrons were emitted from CNFs using the extraction voltage and accelerated toward the thin film using the acceleration voltage. VUV CL from the $\text{Nd}^{3+}:\text{LuF}_3$ thin film was emitted through the substrate. A substrate with high transmittance in the VUV region was needed to output light efficiently and MgF_2 , which exhibited 94% transmittance at 180 nm, satisfied this condition. The lamp benefited from a low power consumption and reduced thermal effects when the field electron emitters were used as cold cathodes [33, 34]. The lamp was operated in the vacuum chamber at an average pressure of $8 \times 10^{-5}\text{ Pa}$.

3. Results and Discussion

The thickness and surface morphology of the $\text{Nd}^{3+}:\text{LuF}_3$ thin film was investigated by using scanning electron microscopy (SEM). The thin film contained some droplets with cracks that originate from structural phase transitions. In contrast, the uniform layer was about 15 nm thick without any cracks. The crystallographic properties were also evaluated by using X-ray diffraction. The high and sharp diffraction patterns indicated the well crystallization of the thin film. The detailed data of these evaluations are described in [29].

Figure 2 shows the CL spectra of the $\text{Nd}^{3+}:\text{LuF}_3$ thin film at different acceleration voltages ranging from 1 to 20 kV. The electron beam current was kept at 600 pA during the CL measurements. The spectra showed a dominant peak in the VUV region at 179 nm and two additional emission peaks at

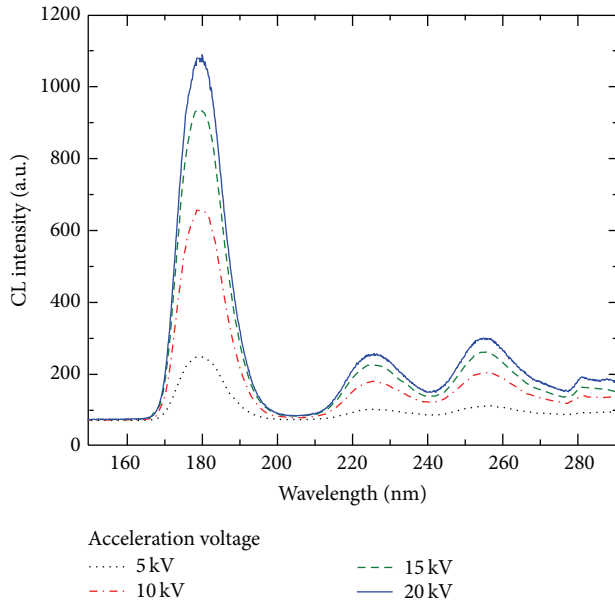


FIGURE 2: CL spectra of the $\text{Nd}^{3+}:\text{LuF}_3$ thin film at acceleration voltages ranging from 1 to 20 kV.

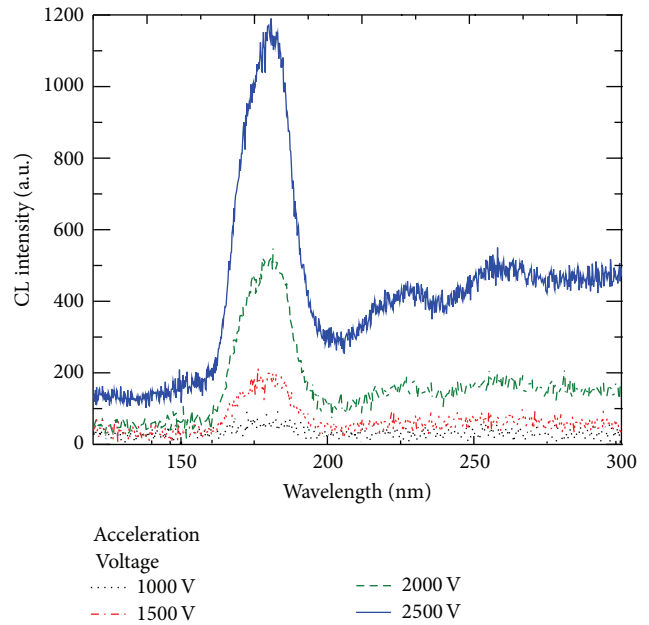


FIGURE 4: Emission spectra of the lamp at acceleration voltages ranging from 1 to 2.5 kV.

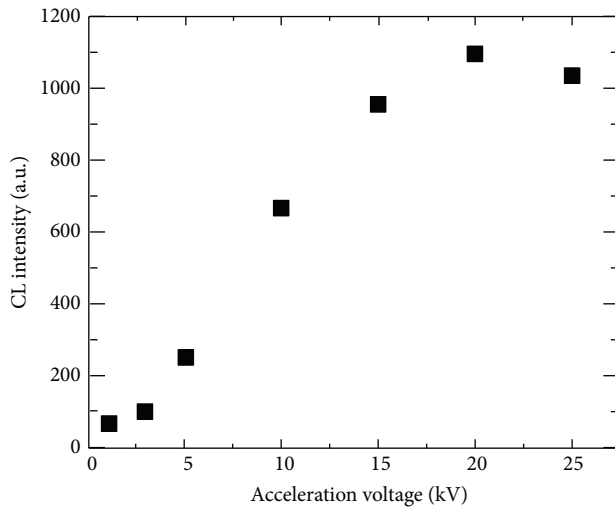


FIGURE 3: Output CL intensity of the $\text{Nd}^{3+}:\text{LuF}_3$ thin film at 179 nm for acceleration voltages ranging from 1 to 25 kV.

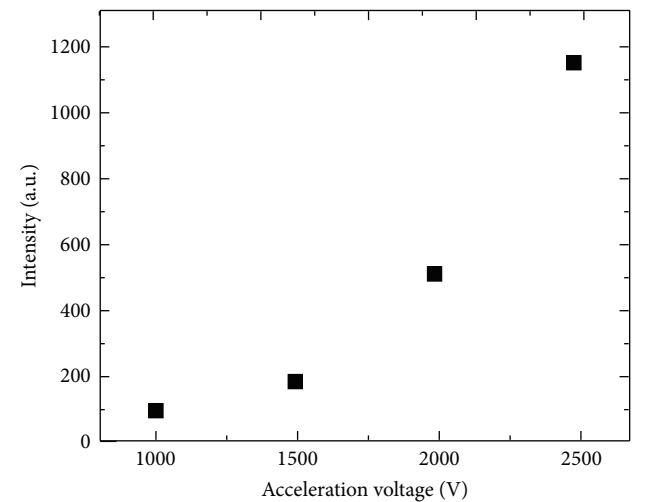


FIGURE 5: Output CL intensity of the lamp at 180 nm for acceleration voltages ranging from 1 to 2.5 kV.

223 and 255 nm, which are consistent with the emission peaks observed for $\text{Nd}^{3+}:\text{LuF}_3$ single crystals [17]. These results show that although the PLD target was obtained by pressing NdF_3 and LuF_3 powders together (undoped material), Nd^{3+} acted as a dopant for LuF_3 and a luminescent center in the thin film.

The influence of the acceleration voltage on the CL intensity of the $\text{Nd}^{3+}:\text{LuF}_3$ thin film at 180 nm was also investigated as shown in Figure 3. The CL intensity increased with increasing acceleration voltage before saturation at 25 kV. This result suggests that incident electrons passed through the thin film before giving all their energy to the thin film at 25 kV.

The emission spectra of the lamp were measured at different acceleration voltages ranging from 1 to 2.5 kV. The extraction voltage was kept at 600 V during the measurements. The emission spectra (Figure 4) presented a dominant peak in the VUV region at 180 nm and two additional peaks at 225 and 255 nm. These spectra closely matched the emission spectra obtained for the $\text{Nd}^{3+}:\text{LuF}_3$ thin film.

The influence of the acceleration voltage on the CL intensity of the lamp at 180 nm was evaluated. The CL intensity (Figure 5) showed a nonlinear dependence on the acceleration voltage, which was attributed to an increase of the electron diffusion region in the thin film. The output

power of this lamp may amount to several microwatts because $\text{Nd}^{3+}:\text{LuF}_3$ and KMgF_3 show quasiequivalent conversion efficiencies [16]. An increase in acceleration voltage may therefore efficiently enhance the output power of this lamp.

The luminescence area of this VUV lamp can easily generate a large area with little thermal effect and low power consumption by employing a CNF field electron emitter. In addition a solid-state phosphor brings many benefits in the VUV lamp such as safety, longevity, stability, and downsizing.

4. Conclusions

In summary, a VUV field emission lamp consisting of a $\text{Nd}^{3+}:\text{LuF}_3$ thin film as a solid-state phosphor and CNF field electron emitter was fabricated. The CL spectra of the lamp showed multiple emission peaks at 180, 225, and 255 nm, which were in good agreement with emission spectra previously reported for the $\text{Nd}^{3+}:\text{LuF}_3$ crystal. This result suggested that Nd^{3+} ion acted as a luminescent center and doped LuF_3 in the synthesized thin film although the target used during PLD was obtained by pressing NdF_3 and LuF_3 powders into a pellet. Furthermore, the output emission intensity showed a nonlinear response to the acceleration voltage, indicating that an increase in acceleration voltage may significantly enhance this output emission intensity. Although recent gas lamps are improving their performances, this lamp may soon become one of the candidates of VUV light sources. These techniques are essential to numerous applications, such as sterilization, surface cleaning, and synthesis and degradation of chemical material.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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References

- [1] J. R. Vig, "UV/ozone cleaning of surfaces," *Journal of Vacuum Science & Technology A*, vol. 3, p. 1027, 1985.
- [2] L. J. Matienzo, J. A. Zimmerman, and F. D. Egitto, "Surface modification of fluoropolymers with vacuum ultraviolet irradiation," *Journal of Vacuum Science & Technology A*, vol. 12, p. 2662, 1994.
- [3] S. Lerouge, A. C. Fozza, M. R. Wertheimer, R. Marchand, and L. Yahia, "Sterilization by low-pressure plasma: the role of vacuum-ultraviolet radiation," *Plasmas and Polymers*, vol. 5, no. 1, pp. 31–46, 2000.
- [4] J. Wieser, D. E. Murnick, A. Ulrich, H. A. Huggins, A. Liddle, and W. L. Brown, "Vacuum ultraviolet rare gas excimer light source," *Review of Scientific Instruments*, vol. 68, no. 3, pp. 1360–1364, 1997.
- [5] J. Y. Zhang and I. W. Boyd, "Efficient excimer ultraviolet sources from a dielectric barrier discharge in rare-gas/halogen mixtures," *Journal of Applied Physics*, vol. 80, p. 633, 1996.
- [6] A. C. Fozza, A. Kruse, A. Holländer, A. Ricard, and M. R. Wertheimer, "Vacuum ultraviolet to visible emission of some pure gases and their mixtures used for plasma processing," *Journal of Vacuum Science and Technology A: Vacuum, Surfaces and Films*, vol. 16, no. 1, pp. 72–77, 1998.
- [7] K. Watanabe, T. Taniguchi, T. Niiyama, K. Miya, and M. Taniguchi, "Far-ultraviolet plane-emission handheld device based on hexagonal boron nitride," *Nature Photonics*, vol. 3, no. 10, pp. 591–594, 2009.
- [8] A. Bergh, G. Craford, A. Duggal, and R. Haitz, "The promise and challenge of solid-state lighting," *Physics Today*, vol. 54, no. 12, pp. 42–47, 2001.
- [9] I. Akasaki, H. Amano, H. Murakami, M. Sassa, H. Kato, and K. Manabe, "Growth of GaN and AlGaN for UV/blue p-n junction diodes," *Journal of Crystal Growth*, vol. 128, no. 1-4, pp. 379–383, 1993.
- [10] I. Akasaki and H. Amano, "Crystal growth and conductivity control of group III nitride semiconductors and their application to short wavelength light emitters," *Japanese Journal of Applied Physics*, vol. 36, no. 9A, p. 5393, 1997.
- [11] W. M. Yim, E. J. Stofko, P. J. Zanzucchi, J. I. Pankove, M. Ettenberg, and S. L. Gilbert, "Epitaxially grown AlN and its optical band gap," *Journal of Applied Physics*, vol. 44, no. 1, pp. 292–296, 1973.
- [12] E. Silveira, J. A. Freitas, S. B. Schujman, and L. J. Schowalter, "AlN bandgap temperature dependence from its optical properties," *Journal of Crystal Growth*, vol. 310, no. 17, pp. 4007–4010, 2008.
- [13] T. Oto, R. G. Banal, K. Kataoka, M. Funato, and Y. Kawakami, "100 mW deep-ultraviolet emission from aluminium-nitride-based quantum wells pumped by an electron beam," *Nature Photonics*, vol. 4, no. 11, pp. 767–771, 2010.
- [14] S. Koizumi, K. Watanabe, M. Hasegawa, and H. Kanda, "Ultraviolet emission from a diamond pn junction," *Science*, vol. 292, no. 5523, pp. 1899–1901, 2001.
- [15] T. Nishimatsu, N. Terakubo, H. Mizuseki et al., "Band structures of perovskite-like fluorides for vacuum-ultraviolet-transparent lens materials," *Japanese Journal of Applied Physics 2: Letters*, vol. 41, no. 4, pp. L365–L367, 2002.
- [16] S. Ono, R. El Ouenzerfi, A. Quema et al., "Band-structure design of fluoride complex materials for deep-ultraviolet light-emitting diodes," *Japanese Journal of Applied Physics*, vol. 44, no. 10, pp. 7285–7290, 2005.
- [17] P. J. Key and R. C. Preston, "Magnesium fluoride windowed deuterium lamps as radiance transfer standards between 115 and 370 nm," *Journal of Physics E: Scientific Instruments*, vol. 13, no. 8, p. 866, 1980.
- [18] Y. Hatanaka, H. Yanagi, T. Nawata et al., "Properties of ultra-large CaF_2 crystals for the high NA optics," in *Optical Microlithography XVIII*, vol. 5754 of *Proceedings of SPIE*, 2005.

- [19] T. Kozeki, Y. Suzuki, M. Sakai et al., "Observation of new excitation channel of cerium ion through highly vacuum ultraviolet transparent LiCAF host crystal," *Journal of Crystal Growth*, vol. 229, no. 1, pp. 501–504, 2001.
- [20] A. Yoshikawa, T. Yanagida, Y. Yokota et al., "Single crystal growth, optical properties and neutron response of Ce³⁺ doped LiCaAlF₆," *IEEE Transactions on Nuclear Science*, vol. 56, no. 6, pp. 3796–3799, 2009.
- [21] N. Kawaguchi, T. Yanagida, A. Novoselov et al., "Neutron responses of Eu²⁺ activated LiCaAlF₆ scintillator," in *Proceedings of the IEEE Nuclear Science Symposium Conference Record (NSS/MIC '08)*, pp. 1174–1176, Dresden, Germany, October 2008.
- [22] R. Visser, P. Dorenbos, C. W. E. van Eijk, A. Meijerink, and H. W. den Hartog, "The scintillation intensity and decay from Nd³⁺ 4f²5d and 4f³ excited states in several fluoride crystals," *Journal of Physics: Condensed Matter*, vol. 5, article 8437, 1993.
- [23] S. Ono, Y. Suzuki, T. Kozeki et al., "High-energy, all-solid-state, ultraviolet laser power-amplifier module design and its output-energy scaling principle," *Applied Optics*, vol. 41, no. 36, pp. 7556–7560, 2002.
- [24] R. W. Waynant and P. H. Klein, "Vacuum ultraviolet laser emission from Nd³⁺:LaF₃," *Applied Physics Letters*, vol. 46, p. 14, 1985.
- [25] M. Yanagihara, M. Z. Yusop, M. Tanemura et al., "Vacuum ultraviolet field emission lamp utilizing KMgF₃ thin film phosphor," *APL Materials*, vol. 2, no. 4, Article ID 046110, 2014.
- [26] K. Fukuda, S. Ishizu, N. Kawaguchi et al., "Crystal growth and optical properties of the Nd³⁺ doped LuF₃ single crystals," *Optical Materials*, vol. 33, no. 8, pp. 1143–1146, 2011.
- [27] M. Ieda, T. Ishimaru, S. Ono et al., "Optical characteristic improvement of neodymium-doped lanthanum fluoride thin films grown by pulsed laser deposition for vacuum ultraviolet application," *Japanese Journal of Applied Physics*, vol. 51, no. 2, Article ID 022603, 2012.
- [28] A. F. H. Librantz, L. Gomes, S. L. Baldochi, I. M. Ranieri, and G. E. Brito, "Luminescence study of the 4f²5d configuration of Nd³⁺ in LiYF₄, LiLuF₄ and BaY₂F₈ crystals," *Journal of Luminescence*, vol. 121, no. 1, pp. 137–148, 2006.
- [29] M. Ieda, T. Ishimaru, S. Ono et al., "Structural and optical properties of neodymium-doped lutetium fluoride thin films grown by pulsed laser deposition," *Optical Materials*, vol. 35, no. 12, pp. 2329–2331, 2013.
- [30] M. Tanemura, T. Okita, H. Yamauchi, S. Tanemura, and R. Morishima, "Room-temperature growth of a carbon nanofiber on the tip of conical carbon protrusions," *Applied Physics Letters*, vol. 84, no. 19, pp. 3831–3833, 2004.
- [31] M. Tanemura, J. Tanaka, K. Itoh et al., "Field electron emission from sputter-induced carbon nanofibers grown at room temperature," *Applied Physics Letters*, vol. 86, no. 11, Article ID 113107, pp. 1–3, 2005.
- [32] M. Tanemura, T. Okita, J. Tanaka et al., "Room-temperature growth and applications of carbon nanofibers: A review," *IEEE Transactions on Nanotechnology*, vol. 5, no. 5, pp. 587–593, 2006.
- [33] R. C. Che, L.-M. Peng, and M. S. Wang, "Electron side-emission from corrugated nanotubes," *Applied Physics Letters*, vol. 85, no. 20, pp. 4753–4755, 2004.
- [34] Y. Saito, S. Uemura, and K. Hamaguchi, "Cathode ray tube lighting elements with carbon nanotube field emitters," *Japanese Journal of Applied Physics*, vol. 37, no. 3, pp. L346–L348, 1998.