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Ballistic electron effects in nanosilicon and their applications

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Functional properties induced in quantum-sized nanosilicon relate not only to photonics, but also to electronics, acoustics, and biology. Among them, the generation of ballistic electrons in nanosilicon extends its usefulness to various applications [1]. The topics on this effect are discussed here.

The nanosilicon cold cathode is a kind of MIS diode consisting of a thin film surface electrode, an anodized nanosilicon layer, crystalline silicon substrate, and a back contact. Nanosilicon dots are interconnected with tunnel oxides. Under an applied voltage of 15-20 V, electrons injected from the substrate into the nanosilicon layer are drifted toward the outer surface and emitted as quasi-ballistic electrons with mean energies of 5-7 eV [2]. The underlying physics of the ballistic transport was clarified by a theoretical modeling of the electron scattering rate in nanosilicon dots [3] and by a statistical calculation.

Physical and electrochemical effects observed in the ballistic electron emission are summarized in Table 1. In vacuum, this device is applicable to the exposure source for parallel EB lithography [4]. Using the device with patterned emission windows, periodic submicron patterns were uniformly delineated over the area of 2.8 mm square by one shot exposure. Another application in vacuum is a probing source for a high-sensitivity image pick-up.

The usefulness of the nanosilicon ballistic emitter in atmospheric gases has been demonstrated as a negative ion source in air and a vacuum-ultraviolet (VUV) light generator in Xe gases. The former is based on the dissociative electron attachment on oxygen molecules. In the latter case, the electron incidence into Xe gas molecules gives rise to direct internal excitation followed by VUV light emission without any impact ionizations.

Table 1. Ballistic electron effects in nanosilicon.

Functions	Media	Possible Applications
Emission	Vacuum	Parallel lithography Image pick-up
	Air	Latent image formation
	Gas (Xe)	VUV emission
Reduction	Aqueous Solutions	H_2 generation Control of pH and H2 content
	Salt Solutions	Thin film deposition of metals, Si, and Ge
Photonic	In-situ	Avalanche photoconduction Advanced PV cell
		Ballistic lighting

In pure water and aqueous solutions, this emitter acts as a supplier of highly reducing electrons [15] leading to the H_2 gas generation through direct reduction of H^+ ions at the emitting surface without using any counter electrodes. This effect is useful for control of the electrochemical properties: pH value and dissolved H_2 content.

The activity in solutions is applicable to thin metal film deposition. It has been demonstrated that by driving the device alone in metal-salt solutions, thin metal (Cu, Ni, Co, Zn, and so on) films can be deposited on the emission area. In addition, the emitter operation in $SiCl_4$ and $GeCl_4$ solutions make it possible to deposit thin amorphous Si and Ge films uniformly by unilateral electro-reduction [5]. Despite a relatively large electrochemical window of $SiCl_4$ and $GeCl_4$ solutions, injected energetic electrons can directly reduce Si^{4+} and Ge^{4+} ions at the interface with neither contaminations nor byproducts. The observed deposition rate, comparable to the conventional dry process, is consistent with the value expected from the emission current density. It has been difficult to get uniform thin Si and Ge films by usual electroplating based on the exchange of thermalized electrons. The ballistic electro-reduction is an alternative low-temperature clean process possibly applicable to the fabrication of various thin film devices.

The generation of ballistic electrons can be used inside the nanosilicon layer. One possible phenomenon is photo-carriers multiplication by impact ionization in nanosilicon dots. Actually, the photoconduction effect has been studied for oxidized nanosilicon dot diodes under reverse bias voltages. The nanosilicon layer shows a significant photoconductive property in the range of visible to near-uv wavelengths. The photoconduction quantum efficiency rapidly increased with increasing the external electric field and reached 2500% at an electric field of 9×10^5 V/cm at 77 K [6]. The experimental data on the temperature, electric field, and sample thickness dependencies of the photocurrent suggest that the high quantum efficiency is due to the field-induced avalanche multiplication of photo-excited carriers inside the nanosilicon dot layer. In accordance with theoretical analyses of carrier dynamics, hot electrons generated at the early stage of injection contribute to sequential impact ionizations [7]. It was clarified that both the onset electric field and the multiplication factor depend on the effective band gap and the population of quantized electron levels in nanosilicon dots, and that the impact ionization rate in nanosilicon dots is significantly higher than that in bulk silicon. These effects are important for the development of efficient photo-sensors and photovoltaic cells.

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References

1. N. Koshida, T. Ohta, B. Gelloz, and A Kojima, Current Opinion in Solid State and Mater. Sci. **15**, 183 (2011).
2. N. Koshida, X. Sheng, and T. Komoda, Appl. Surf. Sci. **146**, 371 (1999).
3. N. Mori, H. Minari, S. Uno, H. Mizuta, and N. Koshida, Appl. Phys. Lett. **98**, 062104 (2011).
4. N. Ikegami, T. Yoshida, A. Kojima, H. Ohyi, N. Koshida, and M. Esashi, J. Micro/Nanolithography, MEMS, and MOEMS **11**(3), 031406 (2012).
5. T. Ohta, R. Mentek, B. Gelloz, N. Mori, and N. Koshida, ECS Trans. **50**, No. 9, "SiGe, Ge, and Related Compounds 5: Materials, Processing, and Devices", pp. 691-698 (2012).
6. Y. Hirano, K. Okamoto, S. Yamazaki, and N. Koshida, Appl. Phys. Lett. **95**, 063109 (2009).
7. N. Mori, H. Minari, S. Uno, H. Mizuta, and N. Koshida, Jpn. Appl. Phys. **51**, 04DJ01 (2012).