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Step Back for Going Beyond

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Abstract

In this talk, we pick up three materials, Ge, HfO_2, and VO_2. These three materials have been studied for a long time but still provide exciting research aspects exhibiting new functional properties, which will hopefully add new values to the next generation electron devices. It is important to recognize their potential with great fun, even though the material in itself is not really new.

I. Introduction

30 years have passed since I gave a talk at SSDM for the first time [1]. I have been mainly involved in gate stack related technology. In this talk, however, we would like to discuss about three materials issues, Ge, HfO_2, and VO_2. Most of you would comment that those are *old* materials investigated in the past. But they are still quite interesting to study and quite new to us. The plenary speakers usually talk about their remarkable outputs carried out up to the present. I would like to, however, challenge to take this opportunity for discussing about materials still open to debate. I believe that a number of materials studied in the past are still like treasure islands to enjoy the research for going beyond.

II. Fixed functionality at metal/Ge interface

Ge is certainly *not new*. In fact, quite interesting Ge papers with deep investigation was reported 100 years ago [2]. In addition, we have been working for high performance Ge CMOS very hard for a decade. In this talk, however, we will not talk about gate stack technology, but would discuss about the Fermi-level pinning (FLP) at metal/Ge interface.

I have been long interested in FLP since I started the professional carrier in the semiconductor technology. But, since so many great seniors had already proposed brilliant models to explain the phenomena and so many other interesting issues to study were in Si technology, I had hesitated to investigate it elaborately. Meanwhile, after we started working for Ge, we encountered this issue again as one of the most serious challenges in Ge MOSFETs, in particular n-channel MOSFETs [3], because the FLP on Ge makes the low ohmic contact resistance impossible. Such a strong negative impact on Ge n-FETs has encouraged us to study about the FLP harder than before [4]. We conjectured the FLP mechanism at metal/Ge interface was derived from an "intrinsic" origin, because metal and its interface properties seemed to actually have nothing to do with the Schottky barrier height. Among models reported in literatures, metal-induced gap states (MIGS) model has the purely intrinsic origin [5]. Thus, we have been willingly "trapped" by the beauty of MIGS.

Two attempts were made to manipulate the FLP from the viewpoint of the suppression of electron wave function evanescent inherent in MIGS. One was the insertion of a tunnel-oxide into metal/Ge interface [6], and the other was to employ the low electron density metals [7]. Both should definitely reduce the wave function evanescent, though other extrinsic effects might be included as well. Both were experimentally quite successful for the FLP alleviation. Now we can make the ohmic contact to n-Ge without any doping. Those experimental facts strongly support the MIGS model for the FLP at metal/Ge interfaces. Even "intrinsic" phenomenon can be tuned.

III. Hard functionality in HfO_2

People involved in Si technology should know HfO_2 as the high-k gate dielectric film since the intel 45 nm technology [8]. The first proposal of using HfO_2 for electron devices was for DRAM MIM capacitors 30 years ago [9]. HfO_2 as the material was rather old, because it is in the family of ZrO_2. Although we have worked for high-k HfO_2 for more than 15 years, I would like to discuss about ferroelectric HfO_2 rather high-k gate stacks.

Why HfO_2 becomes ferroelectric? It is said that the orthorhombic phase of HfO_2 might be responsible for ferroelectric phase formation of HfO_2 [10], while the monoclinic HfO_2 is used for the high-k gate dielectric film. The doping is the key to the manifestation of ferroelectric properties, and many kinds of cation doping can actually make HfO_2 ferroelectric. Even the anion (N) doping can make it as well [11]. Therefore, we infer the dopant may play two roles, physically (structural tolerance and bonding constrain) and chemically (charge balance), in the ferroelectric phase formation [12].

Ferroelectric materials have been already studied quite intensively and are partly used in FeRAM. What's new in ferroelectric HfO_2? In case of HfO_2, physical thickness can be reduced down to a few nanometer-thick level, while in perovskite ferroelectric films, it is hard to achieve nanometer range of thickness keeping ferroelectric properties. It is a big difference between HfO_2 and conventional perovskite ferroelectric materials. So, we are interested in the ferroelectric tunnel junctions (FTJs). The idea of FTJ function which utilizes the tunneling current modulation in conjunction with the polarization switching was proposed in 1971 [13]. But it has not been intensively studied so far [14]. Therefore, we think ferro-

electric HfO_2 has a big chance for FTJ applications.

3-nm-thick Y-doped HfO_2 was deposited on TiN, followed by PDA. The HfO_2 FTJ successfully exhibits more than two orders of resistance change [15]. Meanwhile, it is hard to confirm the ferroelectricity in the tunneling oxide region. The piezo-response force microscopy (PFM) helps us to verify the ferroelectricity of a few nanometer-thick films [16]. I-V characteristic in FTJ looks like the bipolar type ReRAM, but there is a distinct difference between them in terms of no conductive filament formation. FTJ characteristics obtained so far are not at the practical application stage, but plenty of room is left for the improvement of junction properties including electrode material engineering. Moreover, the two-terminal operations with non-linear I-V characteristics in FTJs will also be potentially attractive for neuromorphic devices.

IV. Soft functionality in VO_2

VO_2 is called as the Mott insulator and exhibits the metal-insulator-transition around the room temperature [17]. Although this peculiar behavior was studied by many researchers in the past, it is still open to debate whether it is really the Mott transition or the Peierls transition. Therefore, it is definitely exciting for us to investigate the field-effect metal-insulator-transition (FE-MIT) to clarify whether only electron accumulation may drive the Mott transition or not, as well as to develop potential applications of FE-MIT. The VO_2 film was 6-nm-thick and epitaxially grown on single crystalline TiO_2. The VO_2 FE-MIT shows that the electric conductivity exponentially increases with the gate voltage increase [18]. This fact suggests that VO_2 in principle shows the electron density triggered MIT, resulting in the structural change from monoclinic (insulator) to tetragonal (metal phase). Furthermore, we found that the phase transition transient had two kinds of time constants [19]. One was fast, and the other was very slow. We conjecture that the fast one might be from the electronic transition, while the slow one through the electron-phonon interaction. If it is the case, the pure Mott transition might have been observed for the first time by the gating.

The key feature of the Mott transition in VO_2 is with only a very small bi-stable barrier. Therefore, in two-terminal VO_2 devices, I-V characteristic exhibits hysteresis in the voltage sweeping, but the resistance goes back to the initial state at zero bias. This is quite different from other memristive devices such as ReRAM, PCRAM or FTJ. Although it is difficult to distinguish between electronic and Joule heating effects in two-terminal devices, nonlinear transport property seems to be more useful in analog than in digital applications. We infer that it will be likely for practical applications in neuromorphic or IoT devices, because adjustable threshold switching can be achieved only by the simple two-terminal geometry [20].

V. Conclusion and future outlook

We have discussed three kinds of popular materials, Ge, HfO_2, and VO_2. Each function observed in these materials is derived from the bi-stability inherent in materials or interfaces. The wave-function evanescent realizes the mono-stable state of the directional dipole formation in metal/Ge interface, while the strong bi-stable polarization occurs in a few nm-thick ferroelectric HfO_2. Gated Mott transition is observed in VO_2 with a small bi-stability barrier.

These materials are well known, but show rather remarkable functional properties than expected, depending on the bi-stability strength. In addition, they provide us with great opportunities to think about materials science and engineering and to develop even new devices. Such material-based functions will hopefully have a connection with versatile electron devices and systems in the next generation.

Although it goes without saying that something really new is important in the research, *old* materials studied in the past may also exhibit really *new* features. *New* does not necessarily mean *new* in the timeline. You may find out a number of *new* opportunities next to you, even though they look small things. In that sense, we occasionally need to *step back for going beyond by carefully looking at details of things*.

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References

[1] A, Toriumi and M. Iwase, SSDM (1987), p. 347 & p. 351.
[2] C. C. Bidwell, PR **19**, 447 (1922).
[3] A. Dimoulas et al., APL **89**, 252110 (2006).
[4] T. Nishimura et al., SSDM (2006), p. 400.
[5] W. Mönch, "Semiconductor Surfaces and Interfaces," 3rd ed. (Springer, Berlin 2001).
[6] T. Nishimura et al., APEX **1**, 051406 (2008).
[7] T. Nishimura et al., (this conference).
[8] M.T. Bohr et al., IEEE Spectrum, 1 Oct. (2007).
[9] K. Yamada, SSDM (1986), p. 257.
[10] T. S. Böscke et al., APL **99**, 102903 (2011)
[11] L. Xu et al., APEX **9**, 091501 (2016).
[12] L. Xu et al., (this conference).
[13] L. Esaki et al., IBM Tech. Discl. Bull. **13**, 2161 (1971).
[14] A. Chanthbouala1 et al., Nat. Nano. **7**, 101 (2012).
[15] X. Tian et al., (this conference).
[16] S. Shibayama et al., VLSI Tech. Symp. (2016), p. 152.
[17] F. J. Morin, PRL**3**, 34 (1959).
[18] T. Yajima et al., Nat. Comm. **6**, 10104 (2015).
[19] T. Yajima et al., (this conference).
[20] Y. Zhou and S. Ramanathan, Proc. IEEE **103**, 1289 (2015).