RoHS Exemption 7c-IV – Response To Oeko

Date of submission: September 15, 2015

1st Questionnaire (Clarification Questionnaire) Exemption No. 7c-IV (renewal request and scope clarification)

Received from Otmar Deubzer on 4-Aug-2015

Exemption for „Lead in PZT based dielectric ceramic materials for capacitors which are part of integrated circuits or discrete semiconductors"

PZT: Lead Zirconium Titanate

Questions

1) Please provide information on the research you conducted since the last review in 2010/2011 on the substitution or elimination of lead in the above requested exemption.

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With support from:

Communications and Information network Association of Japan (CIAJ)	
European Coordination Committee of the Radiological, Electromedical and Healthcare IT Industry (COCIR) ID Number – 05366537746-69	
DIGITALEUROPE ID number: 64270747023-20	

European Ceramic Industry Association (Cerame-Unie) ID number: 79465004946-12	
European Committee of Domestic Equipment Manufacturers (CECED) ID number: 04201463642-88	
Electronic Components Industry Association (ECIA)	
European Garden Machinery Industry Federation (EGMF) ID number 82669082072-33	
European Passive Components Industry Association (EPCIA) ID number: 22092908193-23	
European Partnership for Energy and the Environment (EPEE) ID number: 22276738915-67	
European Semiconductor Industry Association (ESIA) ID Number: 22092908193-23	
Information Technology Industry Council (ITI) ID Number : 061601915428-87	
IPC – Association Connecting Electronics Industries	
Japan Business Council in Europe (JBCE) ID number: 68368571120-55	
Japan Business Machine and Information System Industries Association (JBMIA) ID number: 246330915180-10	
Japan Electronics and Information Technology Industries Association (JEITA) ID number: 519590015267-92	

Japan Electrical Manufacturers´ Association (JEMA)	JEMA
LightingEurope ID number 29789243712-03	LIGHTINGEUROPE THE VOICE OF THE LIGHTING INDUSTRY
Zentralverband Elektrotechnik- und Elektronikindustrie e. V. (ZVEI) ID number is 94770746469-09	ZVEI: Die Elektroindustrie
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Answers provided below do not contain confidential or proprietary information.

Answers

1) Preamble

The integrated circuits or discrete semiconductors involving PZT based dielectric ceramic materials for capacitors are mainly, but not limited to:

- IPD: Integrated Passive Devices, including functional blocks such as impedance matching circuits, harmonic filters, couplers, baluns and power combiner/divider, generally fabricated using standard wafer fab technologies such as thin film and photolithography processing, realized on thin substrates like silicon, alumina or glass. IPD technology enables high-density capacitors, MIM capacitors, resistors, high-Q inductors, PIN diodes or Zener diodes to be integrated on the same silicon. These passives combined with active functions in one component respond to the high integration and low power consumption featured by high performing wireless devices.

- FeRAM or FRAM: Ferroelectric Random Access Memory, are a random-access memory similar in construction to DRAM but using a ferroelectric layer instead of a dielectric layer to achieve non-volatility. FeRAM is one of a growing number of alternative non-volatile random-access memory technologies that offer advantages over flash memories including lower power usage, faster write performance and a much greater maximum number of write-erase cycles. FeRAM products are found in a variety of sectors including (but not limited to) electricity meters, automotive electronics, business machines, instrumentation, medical equipment, industrial microcontrollers, and radio frequency identification tags.

2) **The exceptional properties of PZT**

As expressed in the dossier submitted on 16-Jan-2015, PZT offers:

- marked piezoelectric effect,
- high dielectric constant, especially large at morphotropic phase boundary,
- pyroelectric behaviour,
- ferroelectric property.

The use of PZT in IPDs is directly linked to its exceptional dielectric constant when used to achieve high density capacitors in thin film, placing this material above any other material in the present state of our knowledge.

In FeRAMs, PZT is used as a typical ferroelectric material, bringing a unique crystal structure, with two stabilization points for zirconium and titanium in the lattice when moving between the points according to the external electric field. FRAM has many benefits compared to standard Flash memory (www.ti.com/fram). Some of the key benefits of FeRAM using PZT are low voltage operation (1.35 Vmin), 10 year 125C reliability and near-infinite write endurance (10^{15}). No other ferroelectric material other than PZT has demonstrated these key benefits.

3) **Current status of PZT used for thin film high density capacitors**

As in 2010-2011, basic research has not evidenced a new material which could substitute to PZT for high density capacitors, so that no alternative to PZT is currently known for thin film capacitors that achieves the same combination of high dielectric constant, high breakdown field and temperature stability of 20% in a temperature range from -25 to +85 °C, this combination of properties being indispensable to realize capacitors as parts of integrated circuits and discrete semiconductors.

In the search for alternative technologies, no feasible substitutes exist either at present. As expressed in the former dossiers submitted for this exemption, trench capacitors have a breakdown of only < 30V, and no MIM is possible. Other potential alternatives such as Barium-Strontium-Titanate (BST) have only half the dielectric constant and result in much larger devices and won't meet the size dimensions of applications. Performance characteristics with alternatives are severely degraded. These potential alternative techniques (trench- or BST-capacitors) are not able to fulfil the electric requirements that are needed for such applications, a high breakdown voltage and low internal resistance at low leakage currents and high capacitance values.

Further studies conducted by one company since 2011 have confirmed what is stated above:

- at equal thickness of the dielectric, BST has a much lower capacity density than PZT,
- when BST thickness is reduced at its minimum, it is possible to catch up PZT in terms of capacitance density, but the reliability is then much below what is expected for the targeted electronic applications,
- with respect to trench capacitances, e.g. a 3-dimension structure, it is possible to obtain comparable densities, but with two parameters affected:
    - o higher series resistance: for density lower than 45 nF/mm^2, PZT and 3D capacitor have almost the same series resistor (Rs), but around and above 45 nF/mm^2, dielectrics must be stacked in trench, in the case of 3D capacitors. This stacking induces an increase of Rs (from x 2 up to x 10 depending on the layout), that can be very damaging for the frequency answer and that can increase the current going through the capacitor during an ESD pulse, conducting to an earlier fuse or breakdown of the device.

- o lower breakdown voltage: for capacitance with medium density (~ 30 nF/mm²), the VBD is around 2 or 3 times lower for 3D capacitor than for PZT capacitors (30V versus 70V). For applications using DC voltage like ADSL, PZT capacitors do not require very low voltage ESD clamping diodes in parallel to be correctly protected, at the contrary of 3D capacitors. If required, a basic protection diode can then be integrated on the same die than the PZT capacitance, improving the frequency answer at reduced cost.

These considerations lead to a quite different parametric compromise than PZT, requiring the re-design of the complete electronic functions.

Concluding Statement:
Most electronic needs tend to be compatible with 3D capacitances when the acceptable breakdown voltage is low and the series resistance high, but there are still applications demanding high voltage or low resistance which cannot be met without PZT (ADSL decoupling capacitor, analogic microphone filters etc.). For those applications, a new material without Pb will have to be invented.

4) Current status of PZT used for FeRAMs

Investigation is reported to have been conducted into the possibilities of eliminating lead (Pb) from the current products. While previous extensive research has ruled out the use of the early-touted lead-free material strontium bismuth tantalite (SST), current investigation involves close monitoring of progress of the alternative lead-free ferroelectric material hafnium oxide, as recently reported by the combined groups at Dresden consisting of NaMLab, Fraunhofer CNT and Global Foundries.

Technical analysis of the Dresden results:

1. The discovery of ferroelectricity in crystalline hafnium silicon oxide was reported by the Dresden group in 2011. (Ferroelectricity in hafnium oxide: CMOS compatible ferroelectric field effect transistors, Electron Devices Meeting (lEDM), 2011 IEEE International P24.5.1 - 24.5.4). Note:

   A Taiwan group is reporting ferroelectricity in a similar system of materials in a similar MFIS FeFET structure. Performance is similar to the Dresden report. (Low-Leakage-Current DRAM-Like Memory Using a One-Transistor Ferroelectric MOSFET with an Hf-Based Gate Dielectric, Cheng and Chin, IEEE Electron Device letters, Vol. 35, No. I, January 2014).
2. The evidence seems incontrovertible that the Dresden team has an embodiment with a memory window. Although Si02:Hf02 may be a ferroelectric in a MFM structure, there is no evidence to show it will be ferroelectric in other than a gate stack. This would need to be accomplished before full productization can occur.
3. The competitive landscape with regard to the hafnia-based FeFET is based on performance. This is summarized in the table below and discussed further below.

	Endurance	Retention	Speed	
			Program /Erase	Read
FRAM (l30nm) FM22LDI6, 4Mbit, parallel	10^{14} cycles	10 yrs/85° C	55-ns access time	55-ns access time, 110-ns 4 Mbit
FeFET (Desden) (32 mm)	10^{4} cycles	10 yrs/25° C	100 ns?	<50ns?
FeFET (Expect)	Same as FRAM ?	Same as FRAM ?	100 ns?	<50ns?

a. Retention: the confidence level of the extrapolated 10 year data retention is low because it is based on 240 hrs room temperature. Extended bakes at higher temperature will help to increases the confidence level and verify that the extrapolation is indeed linear with log time. The Dresden lead technologist agrees with this evaluation that retention is limited.

b. Endurance: this FeFET technology will not replace the FRAM performance as most applications require very high endurance. The endurance is clearly inferior to current FRAM. This FeFET would be far too slow and die almost instantly in most applications.

c. The characterization of the current FeFET devices is interesting but more work needs to be done. The distribution of individual devices would be very interesting and, if anything like typical memory weak bit issues, could require a significant amount of work to control. The anomalous behavior seen on the 32nm devices may be a side effect of the channel implants; so more work is needed to prove there is not a fundamental limitation of ferroelectric HfD2 at these geometries. We expect and hope the Dresden group proceeds on this issue.

d. It is not sure that a higher coercive voltage is advantageous as claimed. To compete with existing floating gate technology, the required ferroelectric layer for the FeFET is so thin that the applied electrical field will be very high. This will limit the endurance performance of the IT FRAM due to polarization fatigue, which is demonstrated by this paper. The current Dresden films require ~2.5V to fully switch the ferroelectric polarization while the PZT FRAM films saturate polarization at less than 1.35V. In addition the Dresden films polarization saturation behavior does not improve at thinner films making it currently impossible to achieve the same low voltage behavior of the PZT.

e. The Dresden group continues to publish based on the original work and good progress is indicated.

Concluding Statement:
It is believed that the Dresden group needs more time to bring this new technology to a product realization capability.

5) Conclusion

Since 2011, the situation of fundamental research in the world has not allowed the R&D departments of companies which design electronic components requiring the exemption 7(c)-IV, to progress toward the substitution or the elimination of lead, while thanks to the unique properties of PZT-based capacitors in ICs or discrete semiconductors, many applications could feature higher integration, extended performance and lower power consumption. Those features are real advantages expected in the development of new electronic devices and, considering the extremely low quantity of lead involved in those components, call for the renewal of the 7(c)-IV exemption.