Exemption Request Form – Exemption 7(c)-IV

Date of submission: January 16, 2015

1. Name and contact details

1) Name and contact details of applicant:

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With support from:

American Chamber of Commerce to the EU (AmCham EU) ID number: 5265780509-97	AmCham EU SPEAKING FOR AMERICAN BUSINESS IN EUROPE
Communications and Information network Association of Japan (CIAJ)	Contraction and Homadon relation of
European Coordination Committee of the Radiological, Electromedical and Healthcare IT Industry (COCIR) ID Number – 05366537746-69	COCIR
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European Semiconductor Industry Association (ESIA) ID Number: 22092908193-23	European Semiconductor Industry Association
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IPC – Association Connecting Electronics Industries	Association Connecting Electronics Industries
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Japan Business Machine and Information System Industries Association (JBMIA) ID number: 246330915180-10	JBMIA
Japan Electronics and Information Technology Industries Association (JEITA) ID number: 519590015267-92	JEITA
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Zentralverband Elektrotechnik- und Elektronikindustrie e. V. (ZVEI) ID number is 94770746469-09	ZVEI: Die Elektroindustrie
Avago Technologies Ltd	

2) Name and contact details of responsible person for this application (if different from above):

Company:	Tel.:	
Name:	E-Mail:	
Function:	Address:	

2. Reason for application:

Please indicate where relevant:

- Request for new exemption in:
- Request for amendment of existing exemption in
- Request for extension of existing exemption
- Request for deletion of existing exemption in:
- Provision of information referring to an existing specific exemption in:
 - Annex III
- 🗌 Annex IV

No. of exemption in Annex III or IV where applicable: 7(c)-IV

Proposed or existing wording:

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

Same as current wording:

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

PZT description:

PZT designates **Lead Zirconium Titanate** which is an intermetallic inorganic compound with the chemical formula Pb[ZrxTi1-x]O3 ($0 \le x \le 1$). It is a white solid that is insoluble in all solvents. Such compound is a ceramic perovskite material that shows the following remarkable properties:

- a marked piezoelectric effect, which finds practical applications in the area of electroceramics
- a **high dielectric constant** especially which can range from 300 to 3850 depending upon orientation and doping, the material featuring an extremely large dielectric constant at the morphotropic phase boundary near x = 0.52
- being pyroelectric, this material develops a voltage difference across two of its faces when it experiences a temperature change. As a result, it can be used as a heat sensor
- it is also **ferroelectric**, which means it has a spontaneous electric polarization (electric dipole) which can be reversed in the presence of an electric field.

Duration where applicable:

We apply for renewal of this exemption for categories 1 to 7, 10 and 11 of Annex I for an additional validity period of 5 years. For these categories, the validity of this exemption may be required beyond this timeframe. Although applications in this exemption renewal request may be relevant to categories 8 & 9, this renewal request does not address these categories. Further, categories 8 & 9 have separate maximum validity periods and time limits for application for renewals.

Other: Background:

While exemption 7c of the Annex to the RoHS Directive would no longer cover the use of Lead in low voltage applications in the 2011 review, an exemption was requested in 2010 since **FRAMS** (Ferroelectric Random Access Memory) and **MIM** (Metal/Insulator/Metal) capacitors using PZT-based dielectric ceramic materials may be operated in the low voltage area. This is the reason of this **recent exemption 7(c)-IV**.

This exemption was justified with the following arguments:

Lead-zirconium-titanate (PZT) material has the highest known dielectric constant (εr = 1000 – 1200) and thus can be used as a planar Metal/Insulator/Metal (MIM) capacitor with a breakdown voltage of more than 100 V. No alternative to PZT is currently known for thin film capacitors and Ferroelectric Random Access Memory (F-RAM) memories 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 is indispensable to realize capacitors as parts of integrated circuits and discrete semiconductors.

- 2) Alternatives to PZT based dielectric ceramic capacitors are not available. Trench capacitors have a breakdown of less than 30 V only, no MIM is possible. Other potential alternatives such as Barium-Strontium-Titanate (BST) have only half the dielectric constant, which results in much larger devices that do not meet the size dimensions of semiconductor applications. Performance characteristics with alternatives are severely degraded. These potential alternative techniques (trenchor 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. New materials without Pb will have to be invented.
- 3) Within the dielectric circuit element of the capacitor, the level of lead content is very low. The amount of lead introduced into the EU per year is in the order of 25-30kg for the considered ROHS applications. Lead in PZT in this case is present in trace amounts.

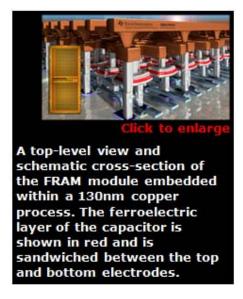
Renewal of Exemption No. 7(c)-IV for thin film PZT deposited on semiconductor

3. Summary of the exemption request / revocation request



devices as stated above.

IPD on silicon - Courtesy of STMicroelectronics



FRAM module - Courtesy of Texas Instruments

Note:

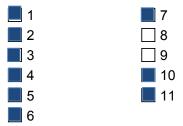
IPD: Integrated Passive Device

FeRAM or FRAM: Ferroelectric Random Access Memory.

4. Technical description of the exemption request / revocation request

(A) Description of the concerned application:

- To which EEE is the exemption request/information relevant? Name of applications or products: Integrated circuits or discrete components that include dielectric ceramic materials for capacitors.
- a. List of relevant categories: (mark more than one where applicable)



b. Please specify if application is in use in other categories to which the exemption request does not refer:

Although applications in this exemption renewal request may be relevant to categories 8 & 9, this renewal request does not address these categories. Therefore, we have not completed section 4(A)1.c. Further, categories 8 & 9 have separate maximum validity periods and time limits for application for renewals.

c. Please specify for equipment of category 8 and 9:

The requested exemption will be applied in

monitoring and control instruments in industry

in-vitro diagnostics

other medical devices or other monitoring and control instruments than those in industry

n/a

2. Which of the six substances is in use in the application/product?

📕 Pb	🗌 Cd	🗌 Hg	Cr-VI	🗌 PBB	PBDE
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3. Function of the substance:

Dielectric material with specific properties for high density capacitors.

4. Content of substance in homogeneous material (%weight):

< 1% of the semiconductor die taken as homogeneous material

 Amount of substance entering the EU market annually through application for which the exemption is requested: < 27.5 kg / year (superior limit)</pre>
Please supply information and calculations to support stated figure.

Calculation:

The Yole production forecast 2012-2018 for **IPD**s, **FeRAM**s and **MEMS** (Micro Electro Mechanical System) combined in number of 6" eq. wafers shipped for the thin film PZT market represents 578,000 (6" eq.) in 2012 and is estimated to be 533,700 (6" eq.) wafers by 2018.

Based on this forecast, a yearly worldwide average estimation over 2014-2020 can be set at **550,000 wfs** (6" eq.) /year, including MEMS.

Estimated weight Pb x 6" wafers: **50 mg maximum** (superior limit)

Estimated weight Pb in devices annually sold to market: $550,000 \times 50 \text{ mg} \sim 27,5 \text{ kg}$ for the worldwide market.

The amount of substance entering the EU market annually through application for which the exemption is requested is much inferior to 27,5 kg while this result applies to the global market, includes the MEMS and bounds from above the mass of PZT deposited on the wafers.

6. Name of material/component:

<u>Material</u>: Lead Zirconium Titanate also called PZT, an intermetallic inorganic compound with the chemical formula Pb[ZrxTi1-x]O3 ($0 \le x \le 1$), see description in paragraph 2.

<u>Components</u>: **Integrated Circuits** or **Discrete Semiconductors** for application categories 1 through 7, 10 & 11 listed in annex I of current ROHS directive.

7. Environmental Assessment:



After the manufacturing process, the PZT is bound in a crystalline and insoluble form. When the components are assembled on the printed circuit board of the application, the PZT will never be released.

According to our current knowledge, the functionality and long lifetime guaranteed for the components made with PZT cannot be achieved with any alternative substance or mixture of substances.

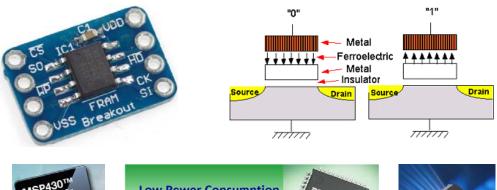
(B) <u>In which material and/or component is the RoHS-regulated substance used</u>, for which you request the exemption or its revocation? What is the function of this material or component?

Pb is present on PZT thin-film technologies such as the examples presented below, including but not limited to capacitors embedded in filters for **wireless devices and other applications** as shown below:



Source: 2013 Yole report "Thin Film PZT for Semiconductor"

Pb is also present in PZT thin-film used for FeRAMs memories as shown below:





	SRAM/DRAM	FLASH E ² PROM	FUJITSU FRAM
Fast Unlimited Read/Write Access	Fast Unlimited R/W Access	Slow Block Access ROM	Fast-Unlimited R/W Access
Non-Volatile	Volatile – Power Required	Non-Volatile	Non-Volatile

Sources: Switch Science, Egloos, Texas Instruments, Cypress Semiconductor, Fujitsu (Internet)

(C) What are the particular characteristics and functions of the RoHS-regulated substance that require its use in this material or component?

PZT is used in **IPDs** for as a very high density dielectric material, with the highest relative dielectric constant of PZT as a processable material.

The **Öko Institute stakeholder 28/07/2010 report** concludes that "technically there are no alternatives for integrated MIM like PZT capacitors. PZT is the only material to integrate highest capacitance density with high breakdown voltages on silicon to ensure best filter- and ESD-performance at low leakage current levels. Trench- and BST-capacitors cannot fulfil the requirements."

PZT is also used in **ferroelectric thin films** deposited on silicon chips for its unique combined properties outperforming existing technologies.

The **Öko Institute stakeholder 28/07/2010 report** states that "only thin film ceramics based on PZT offer the combination of high breakdown voltages, high permittivity and temperature stability to realize silicon integrated capacitors and the ferroelectric advantageous properties of FRAMs. These devices are highly reliable and are easy to manufacture."

PZT based dielectric ceramic materials of capacitors in integrated circuits (ICs)

Specific material properties and uses

The stakeholders (NXP 2009) explain that besides the piezoelectric properties, leadzirconium-titanate (PZT) shows also ferroelectric properties: They are polarized, and the polarization can be reversed by an external electromagnetic field. PZT ceramic thus has the ability to switch polarisation in the electrical field. It has the highest known dielectric constant (k = 1000 – 1200) (ESIA 2006), and a high electrical breakdown voltage of 100 V and more. PZT ceramics therefore are the most effective technical ceramic material to ensure best filter and electrostatic discharge (ESD) performance as required in automotive applications. The PZT based materials in combination with NME (noble metal electrode) only (MIM) meet the ESD performance required in integrated circuits (ICs) or discrete semiconductors. There are no alternative technologies/materials, which can provide the same performance (NXP 2009, ESIA 2006).

And also:

Lead is required to achieve the high dielectric constant of the PZT based applications in semiconductors. The PZT layer is encapsulated by layers of silicon nitrides and oxides, electrode metals and polymer layers. Therefore, the PZT is not exposed to the environment (NXP 2009).

Ferroelectric thin films based on PZT are currently used on silicon chips for (NXP 2009):

- FRAM (ferroelectric random access memories, non-volatile memories;
- low voltage high-density (MIM) capacitors ("high-k") with a breakdown voltage of more than 100 V;

Capacitors store electrical energy in dielectric materials. Two electrodes are used to conduct the energy to and from the capacitor. Figure 64 illustrates the two common capacitor types for integrated capacitors. The silicon substrate can be used as electrode (MIS or MOS). In this case, all capacitors share the substrate as ground electrode. MIM capacitors can be used in any configuration (NXP 2009).

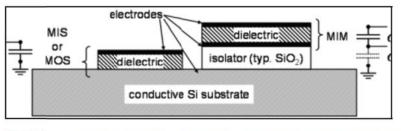


 Figure 64
 Typical thin-film capacitor configurations: MIM and MIS or MOS (NXP 2009)

 MIM
 metal insulator metal

 MIS
 metal insulator semiconductor

 MOS
 metal oxide silicon

Only thin film ceramics based on PZT offer the combination of high breakdown voltages, high permittivity and temperature stability to realize silicon integrated capacitors and the ferroelectric advantageous properties of FRAMs. These devices are highly reliable and are easy to manufacture (Ramtron 2009).

5. Information on Possible preparation for reuse or recycling of waste from EEE and on provisions for appropriate treatment of waste

1) Please indicate if a closed loop system exist for EEE waste of application exists and provide information of its characteristics (method of collection to ensure closed loop, method of treatment, etc.)

Articles object of this exemption are not end products and as such, the manufacturers which are not the manufacturers of the end products, are not directly involved the EEE waste.

Note: Some end products are recycled and/or refurbished. Some materials are dismantled for valuable material collection such as metals, or landfilled.

Currently one third of WEEE in the EU is being reported by compliance schemes as separately collected and appropriately managed (note that some of this might be via destinations outside the Member State of origin).

The remaining WEEE are either:

- 1) collected by unregistered enterprises and properly treated
- 2) collected by unregistered enterprises and improperly treated or even illegally exported abroad or
- 3) disposed of as part of residual waste (e.g. to landfill or incinerators).

Reference: Eurostat

http	://epp.euro	ostat.ec.eu	opa.eu/por	tal/page/	portal/waste/key	waste	streams/wa
ste	electrical	electronic	equipment	weee	-		_

In general there is no closed loop system, just on-customer basis related to specific sectors.

2) Please indicate where relevant:

- Article is collected and sent without dismantling for recycling
- Article is collected and completely refurbished for reuse
- Article is collected and dismantled:
 - The following parts are refurbished for use as spare parts:
 - The following parts are subsequently recycled:

Article cannot be recycled and is therefore:

- Sent for energy return
- Landfilled

Articles object of this exemption are not end products and as such therefore answering to this question is irrelevant

Note: Some EEE are recycled and/or refurbished. Some Equipment are disposed as part of residual waste (e.g. to landfill or incinerators).

3) Please provide information concerning the amount (weight) of RoHS substance present in EEE waste accumulates per annum:

In articles which are refurbished

In articles which are recycled

In articles which are sent for energy return

In articles which are landfilled

Note: while the total content of Lead in EE products put on the worldwide market in 2013 can be estimated at around 9,000 t, the estimated superior limit of Pb in devices with PZT thin film components is **27.5 kg**, representing annually not more than about **3 ppm** of the total weight of Lead introduced on the worldwide market.

6. Analysis of possible alternative substances

(A) Please provide information if possible alternative applications or alternatives for use of RoHS substances in application exist. Please elaborate analysis on a life-cycle basis, including where available information about independent research, peer-review studies development activities undertaken

No possible alternative substance matching PZT dielectric properties can be found in the current state of material physics knowledge.

See section 7(B) and the following reports:

- Öko-institute Final report revised version Freiburg, 28 July 2010: "Adaptation to scientific and technical progress of Annex II to Directive 2000/53/EC (ELV) and of the Annex to Directive 2002/95/EC (RoHS)"
- Yole: "Thin Film PZT for Semiconductor Application trends & Technology update (FeRAM, IPDs and MEMS)" – 2013
- (B) Please provide information and data to establish reliability of possible substitutes of application and of RoHS materials in application

n/a (no possible substitute)

7. Proposed actions to develop possible substitutes

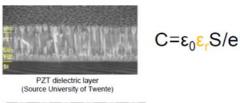
(A) Please provide information if actions have been taken to develop further possible alternatives for the application or alternatives for RoHS substances in the application.

The Yole Thin Film PZT for Semiconductor report, while indicating two alternatives (both identify a new material and develop a new technology), concludes on a trade-off between the capacitance density and the breakdown voltage (see below).

 2 alternative technology tracks are typically followed to integrate high density decoupling capacitors (mainly for decoupling purposes) in Thin Film IPD:

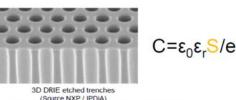
High K planar capacitors:

 High-K ferroelectric materials like PZT or PLZT are deposited in Thin Films so as to form the dielectric of the capacitors



- 3D trench capacitors:

 Deep trenches are etched by micromachining of the silicon substrate, and Thin-Film layers are then conformally deposited in the trenches to form the capacitors. This way, the surface are of the capacitors' electrodes is extended in all 3 dimensions



- In all cases, Thin-Film deposition of the dielectric layer allows for the making of thin capacitor dielectrics.
 - The optimal dielectric thickness is a trade-off between capacitance density and the breakdown voltage

The Öko-institute Final report, concludes for its part:

According to the stakeholders (NXP 2009), PZT based ferroelectric memories have unique properties for mainstream flash and EEPROM chips (NXP 2009):

- low voltage
- low power consumption
- fast write
- high endurance over a broad temperature range

The FRAMS and integrated capacitors based on PZT outperform existing technologies. For both the PZT based integrated capacitors as well as for the FRAMS, market introduction is fairly new. Mass production only started around 2000 (NXP 2009).

(B) Please elaborate what stages are necessary for establishment of possible substitute and respective timeframe needed for completion of such stages.

Substitute materials:

The Semiconductor Industry is working independently with selected material suppliers on the selection of an appropriate replacement for PZT. The properties of the needed capacitance and piezoelectricity material are specified

by the industry (material requirement specification) and provided to the material suppliers. Selected material suppliers offer their materials, which are evaluated by one of the companies together with the suppliers. The combined results are evaluated by the industry. After a material is chosen and material development is frozen, **a minimum of 6 years** will be required to qualify the new material through the whole supply chain. Based on current status, the Semiconductor Industry cannot predict a date for customer sampling. However the Semiconductor industry is already engaged on evaluating different alternative materials and evaluating other in-house material synthesis as well.

Development of BST - Barium Strontium titanate (Ba1-xSrxTiO3) - and SBT -Strontium Bismuth tantalite (SrBi2Ta2O9) - materials in order to solve the RoHs issues with Pb in PZT is considered, but no fixed timeline can be defined. <u>However, SBT and BST have a 2x lower performance than PZT so there is a</u> reluctance to switch to SBT and BST.

	PZT	BST	Requirements
Operating Temperature	-40C to +125C	-10C to +85C	-40C to +125C
Longevity	≥ 40 years	~10 years	>40 years
Endurance	1E12 r/w [1] cycles	1E9 r/w cycles	Unlimited cycles
Relative dielectric K	1700 [2]	500 [3]	Highest Possible

Comparative table between PZT and BST based capacitors (source Texas Instruments):

[1] r/w = read/write

[2] MEMS, Dec 1995, Vol. 4, No. 4, p.234

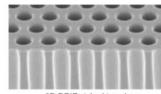
[3] Scott, J.F., "High-dielectric Constant Thin Films for Dynamic Random Access Memories (DRAM)," Annu. Rev. Mater. Sci. 1998. 28:79–100

Substitute technologies:

Trench (MOS) capacitors could be a potential alternative to high-density silicon integrated capacitors.

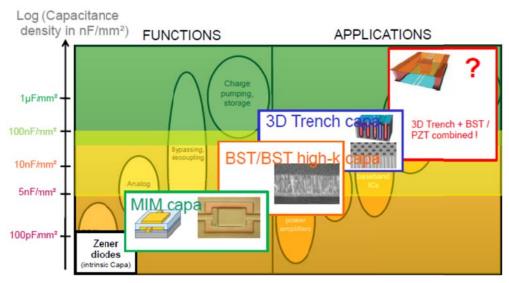
3D trench capacitors:

 Deep trenches are etched by micromachining of the silicon substrate, and Thin-Film layers are then conformally deposited in the trenches to form the capacitors. This way, the surface are of the capacitors' electrodes is extended in all 3 dimensions (Source University of Twente)



3D DRIE etched trenches (Source NXP / IPDiA)





Where Does IPD Technologies Fit in Terms of Density Versus Application?

Source: 2013 Yole report "Thin Film PZT for Semiconductor"

However, according to Yole:

In all cases, Thin-Film deposition of the dielectric layer allows for the making of thin capacitor dielectrics.

 The optimal dielectric thickness is a trade-off between capacitance density and the breakdown voltage

And to the Öko Institute:

According to the stakeholders (NXP 2009, ESIA 2006), however, trench capacitors have

- much lower capacitance density and
- significantly lower breakdown voltage only (30 V, compared to 100 V for PZT-based materials (ESIA 2006)

compared to PZT based capacitors.

The disadvantage of a the lower capacitance density can partially be compensated by using the 3rd dimension making the capacitors larger. However, the stakeholder claims (NXP 2009) that the breakdown voltage of PZT based capacitors cannot be reached and that the MOS trench capacitors thus are not a viable substitute for the PZT based capacitors containing lead. MIM-type high k capacitors cannot be verified without PZT ceramics.

Also, relatively to costs, according to Yole report (page 75), 3D trench technology is an expensive alternative to PZT thin film technology.

Yole conclusions on other piezo materials are:

- There are many ferroelectric and piezoelectric materials available today depending on the application:
 - Most common are : AIN, LiTO₃, BST, SBT, doped PZT (with Mn, La...), PT, ...

- Although many developments on lead-free materials are conducted in the academic world and in the industry, there is no alternative material that matches PZT piezoelectric properties up to now.
- Many developments are being conducted to find an alternative candidate to PZT, but we do not see any clear candidate to enter the semiconductor market before 2018.

8. Justification according to Article 5(1)(a):

(A) Links to REACH: (substance + substitute)

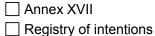
 Do any of the following provisions apply to the application described under (A) and (C)?

Authorisation

SVHC [1]
Candidate list [1]
Proposal inclusion Annex XIV
Annex XIV

[1] Lead Titanium Zirconium Oxide / EC 235-727-4 / CAS 12626-81-2 and Lead Titanium Trioxide / EC 235-038-9 / CAS 12060-00-3.

Restriction



Registration

No registration is required while PZT is produced with the article and/or used by much less than 1 ton/y in the scope of exemption 7cIV (27.5 kg substance used or produced annually by the EU market).

2) Provide REACH-relevant information received through the supply chain. Name of document: None.

(B) Elimination/substitution:

1. Can the substance named under 4.(A)2 be eliminated?

Yes. Consequences?

No. Justification: No substitutes with required properties exist.

See reports stated in section 6. (A) and relayed extracts inserted in this form.

2. Can the substance named under 4.(A)2 be substituted?

🗌 Yes.	
	Design changes:
	Other materials:
	Other substance:
No.	

Justification: No substitutes with required properties exist.

See reports stated in section 6. (A) and related extracts inserted in this form.

- 3. Give details on the reliability of substitutes (technical data + information): n/a
- 4. Describe environmental assessment of substance from 4.(A)1 and possible substitutes with regard to
 - 1) Environmental impacts: n/a
 - 2) Health impacts: n/a
 - 3) Consumer safety impacts: n/a
- Do impacts of substitution outweigh benefits there of?
 Please provide third-party verified assessment on this: n/a

(C) Availability of substitutes:

- a) Describe supply sources for substitutes: n/a
- b) Have you encountered problems with the availability? Describe: n/a
- c) Do you consider the price of the substitute to be a problem for the availability?

Yes No (n/a)

 What conditions need to be fulfilled to ensure the availability? Same physical dielectric and ferroelectric properties.

(D) Socio-economic impact of substitution:

⇒ What kind of economic effects do you consider related to substitution?

No substitute available with similar physical properties

- Increase in direct production costs
- Increase in fixed costs
- Increase in overhead
- Possible social impacts within the EU
- Possible social impacts external to the EU

Other: _____

⇒ Provide sufficient evidence (third-party verified) to support your statement: See reports stated in section 6. (A)

9. Other relevant information

Please provide additional relevant information to further establish the necessity of your request:

No substitute material with equivalent physical properties.

10. Information that should be regarded as proprietary

Please state clearly whether any of the above information should be regarded to as proprietary information. If so, please provide verifiable justification: n/a