

Towards Safer Primers: A Review

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Abstract: Primers are used to reliably initiate a secondary explosive in a wide range of industrial and defence applications. However, established primer technologies pose both direct and indirect risks to health and safety. This review analyses a new generation of primer materials and ignition control mechanisms that have been developed to address these risks in firearms. Electrically or optically initiated metal, oxide and semiconductor-based devices show promise as alternatives for heavy metal percussive primers. The prospects for wider use of low-cost, safe, reliable and non-toxic primers are discussed in view of these developments.

Keywords: primers; semiconductor bridges; thermites; energetic materials

1. Introduction

The evolution of energetic material technology is important and is constantly progressing. Energetic materials typically fall into three categories: explosives that are designed to detonate, propellants that generally deflagrate, or pyrolants that can deflagrate or detonate [1–3]. A detonation is a reaction that propagates faster than the sonic velocity of the material, creating a shock wave at supersonic speeds. Deflagration is the decomposition of a material at velocities much slower than the sonic velocity and is typically thermally propagated.

Explosive materials have proven to be indispensable from the earliest cannons to modern artillery, rockets, airbags, mining and demolition applications. Primers (or detonators more broadly) generally contain small amounts of primary (detonating) explosives that are used to initiate a larger quantity of a high performance, less sensitive material. This combination is important as it is safer than solely using a primary explosive, as these are generally sensitive to stimuli and thus dangerous in large quantities [4].

Due to the major defence and industrial applications, primer technology has largely evolved outside the public domain, following arcane rules defined by national interests and security concerns. Nonetheless there is a natural progression of high impact technologies towards wider use in commercial applications with higher precision and better efficiency than previous generations of technology [5,6]. In this regard, the basic principles and materials have to be well understood in order to meet public safety concerns.

There are many factors that contribute to the need for alternatives to commonly used explosives. Manufacturing of energetic materials is a hazardous process, calling for alternative production methods

that are safer and more efficient [7]. Lead azide ($\text{Pb}(\text{N}_3)_2$) is a common primary explosive used in primers and is of concern due to its lead content [8]. Along with other energetic materials used to initiate explosives and pyrotechnics, the toxicity of these materials and their reaction products is apparent [9–11]. Therefore the concerns for these primer compounds are based on the dangers of handling and manufacturing, their toxicity, and their environmental impact [12–14]. The stability of these compounds is also critically important: potentially fatal malfunctions of air bags in cars using primary explosives has caused harm, where the chemical stability has been compromised by temperature and humidity [15].

Research has brought about modern alternatives for primers that are well established in the industry. Replacement compounds have been identified in a number of promising directions. New environmentally friendly “green” explosives that are heavy metal free and non-toxic provide one avenue. Solid-state energetic devices (igniters) to replace the need for explosive primer compounds is another field of great interest [16–19]. The main purpose of this review is to explore the emerging materials, devices and ignition principles that are underpinning the safer and more controlled use of energetic materials as primers.

2. From Fuses to Flintlocks: Evolution and Use Of Primers

Since its discovery by the Chinese in the ninth century AD and subsequent widespread adoption over the next several hundred years, gunpowder and the high-energy materials that followed have a need for controlled methods of ignition [20,21]. To do so, a stimulus energy from a non-explosive source (e.g., flame, impact or electrical current) needs to be transferred to initiate the main explosive. With early gunpowder-based weapons, the inclusion of a fuse allowed for the time-delayed ignition of the powder. Control over the time of a gunpowder explosion (a longer fuse and/or delay) meant that early grenades and incendiary arrows could be lit, fired and only explode at a target location after some specified time. This precisely controlled, variable delay is realised through a series of reaction steps, called an *explosive train* [4].

The explosive train consists of a series of elements that include, but are not limited to, delay components, booster, transfer or output charges [5]. For gunpowder, a fuse can transfer energy via flame to the gunpowder to cause ignition. In many cases, such as when firing a mortar as shown in Figure 1, it was more appropriate to directly ignite the powder, as delays were not useful. In modern times, direct ignition can be categorised into igniters, which output a flame, and detonators, which output a shockwave.



Figure 1. A 420 mm calibre artillery mortar that fired up to 200 kg projectiles at $200\text{--}250\text{ m}\cdot\text{s}^{-1}$ and an angle of $50\text{--}75^\circ$ to the horizon. Direct ignition of gun powder was used. Biržai Castle, Lithuania; late 16th century, circa 1700.

2.1. Primers

A primer is usually the first component in an explosive train that translates a controlled explosive impulse to the next element, typically a booster or main charge. They are commonly used in firearms and a range of other applications with varying methods of initiation. They can be used with fuse wires in weapons, mining and demolition in military and civilian applications, and in airbags [22]. Primers are commonly made using azide and styphnate based primary explosives, which are sensitive, high nitrogen content compounds, contained in a metal casing, as shown in Figure 2 [5]. These self-contained primer mixes inside a metal case are known as percussion caps due to their simple initiation by mechanical shock. This mechanism, patented by Alfred Nobel in 1867, is an early model of modern primer caps that are largely unchanged in design [23]. These percussion caps are very similar to electric primers as the overall design is simple and can be altered depending on the initiating stimuli [24].

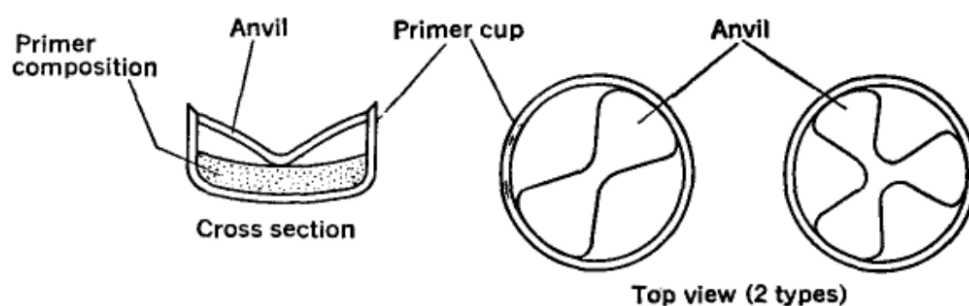


Figure 2. Side and top views of a percussion cap, comprised of the primer cup, anvil and primer mix to house and provide localised impact for initiation [25].

Prior to primary explosives, it was common to see a propellant called *black powder* used as an explosive. The compound standard mixture has varied over time and also depends on the origin but is otherwise roughly 10% sulfur, 15% charcoal and 75% potassium nitrate [26]. On decomposition black powder deflagrates, produces heat and large volumes of fast expanding gas, which under special conditions can transition to detonation. Figure 1 shows a typical early mortar where a direct ignition of black powder was used without primers. A modern day black powder alternative called Pyrodex is one of many possible compounds is used in an explosive train after the primer. Pyrodex is a safer, smokeless and cleaner burning mix that uses additional components along with the standard black powder composition [27].

Propellants and pyrolants can undergo a deflagration-to-detonation transition (DDT) under specific conditions usually induced by a primer detonation in confined space. The DDT of a compound is a process of accelerating the reaction by having the propagation mechanism transition from thermal to shock wave driven [5,28–31]. This process is complex and can come about by high energy shock wave, a mix of shock wave and thermal energy or very high temperature gradients [26,32–35]. This is an advantageous process as only small amounts of primary explosives are needed to induce DDT of a propellant or pyrolant.

The initiating efficiency, high nitrogen density and low production cost of lead azide and lead styphnate makes them attractive for use as primers. However, even with an explosive train mechanism, there is still an issue with using these common primary explosives owing to the danger of handling, misfiring and heavy metal toxicity of the compounds [5,10,11,36]. When decomposed, lead azide produces lead metal which can be detected in residues by various means, such as energy-dispersive X-ray detection and gas chromatography-mass spectroscopy [37–40].

Lead toxicity is a highly studied and important area of research that has raised concerns for health and the environment [11]. Lead can cause noticeable behavioural and cognitive deficits in newborn and young infants at levels as low as 100–150 $\mu\text{g}\cdot\text{L}^{-1}$ in blood [13,41]. Studies on mice exposed to lead azide

by oral intake show negative effects on health, with mortality occurring after prolonged exposure to concentrations greater than 150 mg per kilogram of body weight [42]. Other azides based on alkali or transition metals, such as copper azide, are not recommended as they are highly sensitive and do not meet safety criteria for handling [43,44]. Although lead azide and other primary explosives are used in modern applications, the toxicity of lead and impact of exposure to the environment warrants a need for alternative, “greener” explosives [3].

2.2. What Primers Come Next?

Due to the nature of primers and their applications, much of the research and development in the field is classified. This limits the ability for rapid progress through the collaborative research that exists in the public and unclassified science domain. Nevertheless, significant research and relevant patents on primers from numerous companies have been published over the last century, with the aim of developing safe, stable and non-toxic “green” high energy explosives and initiator devices [5,45–52].

There are some proposed criteria for green primaries, such as low toxicity, chemical stability under light and moisture over extended time periods, thermal stability up to a specified temperature and high initiation efficiency [5,16,36]. For initiating devices called igniters, the idea is to remove the need for primary explosive compounds and instead use energetic reactions or sublimation of materials to generate high temperatures that thermally initiate the next compound in the explosive train. These typically involve the use of reactive metals and oxide materials commonly used as thermites.

Although there have been some review papers on various explosives and green alternatives [16,19,53], none of these have assessed the important progress in solid-state based igniters. Here we review publicly available patents and publications on new methods of ignition that provide a safer alternative to primer compounds for detonators, without the need for primary explosives. As new methods of ignition gain acceptance, it can be expected that new materials and designs will emerge to optimise their efficiency.

3. Materials

Materials that show promise for solid-state igniters include reactive combinations of metals, metalloids and oxides. Thermite mixes consist of materials that undergo exothermic oxidation and reduction reactions, and produce high temperatures and gas by-products [53,54]. Materials are chosen with consideration for their availability and cost, as well as their reaction performance in terms of heat, gas, initiation energy, process rate and device integrability. Fabrication of micrometer-sized devices is a particular focus as they can be manufactured using well-established lithography and deposition techniques commonly used in the semiconductor industry [55,56]. Regardless of the material used, the performance needs to meet the standard required for the application. In the case of primer replacements, it should be capable of inducing a DDT for propellants or other energetic materials used in the explosive train [26].

3.1. Green Energetic Materials

Lead azide and styphnate are very well established in the explosives industry, making the introduction of any new replacement materials difficult [4,57–59]. Some properties of lead azide are detailed in Table 1. While it is not as energetic as pentaerythritol tetranitrate (PETN) or trinitrotoluene (TNT), its performance makes it suitable for use as a primer [25]. An alternative compound to lead azide, copper(I) 5 nitrotetrazolate (DBX-1) has similar performance and ignition properties as shown in Table 1 and is lead-free, which makes it an attractive energetic material [57]. Similarly, a lead-free alternative for lead styphnate, potassium 5,7-dinitro-[2,1,3]-benzoxadiazol-4-olate 3-oxide (KDNP), has been reported and importantly has been qualified as a drop in replacement for military use [58].

Numerous other green energetic materials or methods of manufacture have been suggested. A 'greener' heating method using microwave radiation is said to have greater temperature gradient control [7]. Ionic liquids as a solvent, catalysts in chemical reactions for reducing the amount of waste product in manufacturing, or dinitrogen pentoxide as a replacement for conventional nitrating processes in nitrating synthesis are suggested as more environmentally friendly and efficient methods [7,49]. Finding alternatives for energetic materials also extends to propellants and pyrolants. It is desired that materials do not have perchlorate, barium, lead, cadmium, mercury and other toxic components [50,60]. Other means of 'greener' manufacture aim to reduce waste during production, increase the yield and efficiency of the material synthesis process, and increase safety by reducing any hazardous steps or materials [61,62].

Table 1. Some properties relating to ignition performance and sensitivities of lead azide, lead styphnate, trinitrotoluene (TNT), copper(I) 5 nitrotetrazolate (DBX-1) and pentaerythritol tetranitrate (PETN) explosives [4]¹, [57]², [50]³.

Property	Energetic Material Properties				
	Lead Azide ¹	Lead Styphnate ¹	TNT ¹	DBX-1 ²	PETN ¹
Empirical formula	Pb(N ₃) ₂	C ₆ H ₃ N ₃ O ₉ Pb	C ₇ H ₅ N ₃ O ₆	C ₂ Cu ₂ N ₁₀ O ₄	C ₅ H ₈ O ₁₂ N ₄
Density (g·cm ⁻³)	4.8	3.0	1.654 (molten)	2.584	1.76
Volume of explosion gases (L·kg ⁻¹)	231		825		780
Heat of explosion (kcal·kg ⁻¹)	391	347	871 (H ₂ O gas)	912.2	1398.2 (H ₂ O gas)
Lead block test (cm ³ ·10 g ⁻¹)	110	130	300		523
Detonation velocity, confined (m·s ⁻¹ @ g·cm ⁻³)	5200 @ 4.6	5200 @ 2.9	6900 @ 1.60	7000 ¹	8400 @ 1.7
Deflagration point (°C)	320–360	275–280	300	256–281 est.	>190 req.
Impact sensitivity (N·m)	2.5–4	2.5–5	15	0.04 ¹	3
Friction sensitivity (N)	0.1–1	1.5	>353	0.1 ¹	60
Electrical discharge sensitivity ³ (mJ)	4.7	0.2		3.1	

3.2. Thermites

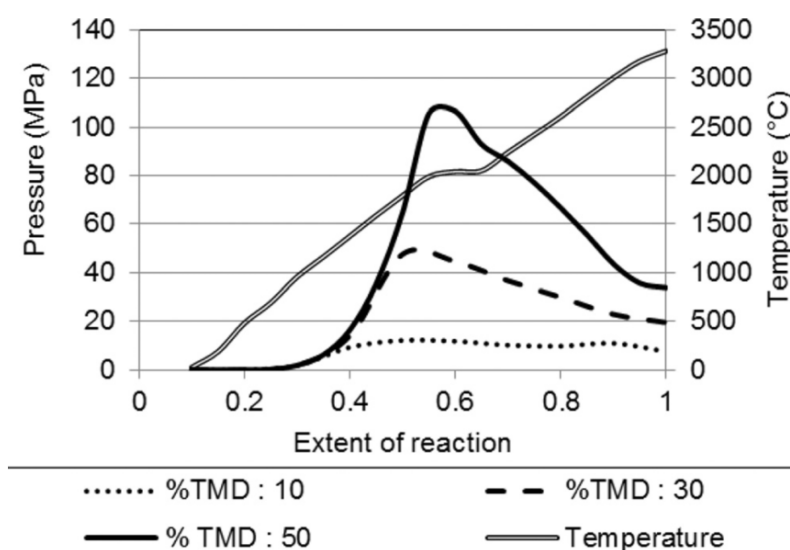
Thermites consist of a reactive metal and a metallic or non-metallic oxide, which can react to release energy in the form of heat at very high temperatures to produce a more stable oxide and metal or non-metal [19,63]. Thermite and intermetallic (e.g., Ti + 2 B) reactions are of interest due to their variation in reaction characteristics such as gas production and heat of reaction. The exothermic reaction of a thermite is able to generate enough heat to create a self-sustaining process. These material combinations are seen in numerous patented devices [64–69].

Table 2 shows a short list of some thermite or metal-metal (intermetallic) materials and their theoretically calculated output temperature, energy and gas production. These reactions are calculated at a stoichiometric ratio and to completion [64]. The upper limit temperature of reaction is calculated by assuming an adiabatic system (no heat lost from the system) with the reactants starting at 298 K. Phase changes are included, together with their heats of transitions and average specific heats over the temperature range. These calculations are a good starting point for determining metal-fuel combinations for a desired reaction parameter.

Gas generating thermite reactions such as Al/CuO in Figure 3, Al/WO₃ and Al/Bi₂O₃ are able to generate theoretical peak pressures of around 110, 150 and 280 MPa respectively. Consequently they are promising candidates for gas pressure wave initiators [65]. The disadvantage is that thermites do not produce as great a volume of gas as the explosives listed in Table 1 and their pressurisation rates are also not as high. A printable aqueous ink of palmitic acid coated aluminium with Bi₂O₃ was measured to have a maximum pressurisation rate of 14.6 kPa/μs and a reaction velocity up to 757 m·s⁻¹ [70,71]. Similarly, an Al/MoO₃ thermite mix was able to generate combustion velocities of 750 and 950 m·s⁻¹ for Al nanoparticle sizes of 120 and 80 nm, respectively [72].

Table 2. Thermite and intermetallic reactions with reaction temperature, gas production and heat of reaction [64].

Thermite and Intermetallic Reactions			
Reactants	Adiabatic Reaction Temperature (K)	Gas Production (L·kg ^{−1})	Heat of Reaction – Q (kcal·kg ^{−1})
2 Al + Bi ₂ O ₃	3253	97.9	506.1
2 Al + 3 CuO	2843	121.0	974.1
2 Al + MoO ₃	3253	54.3	1124
2 Al + WO ₃	3253	32.1	696.4
4 Al + 3 SiO ₂	1889	0	513.3
Ti + 2 B	3498	0	1320
Ti + 2 CuO	2843	72.6	730.5
Ti + SiO ₂	715	0	75.0
Zr + 2 CuO	2843	124.4	752.9
Zr + SiO ₂	1687	0	299.7

**Figure 3.** Theoretical pressures for the Al/CuO thermite reaction at different percentages of theoretical maximum density (% TMD) and equilibrium temperature as a function of the extent of reaction [65].

Although the theoretical gas production value for the Al/CuO thermite in Table 2 is higher than Al/Bi₂O₃, experimental results show higher pressurisation and burning rates for the latter. Uncoated 80–150 nm Al and 100–150 nm Bi₂O₃ nanoparticles were reported to reach even higher pressurisation rates of 5762 kPa·μs^{−1}.

Powdered energetic reactant mixes can be added to initiators with their wide range and tunable reaction rates, temperatures and gas evolution. This depends on multiple factors such as the composition, stoichiometry, particle or layer size for solid-state mixes and distribution (layers, particles, vertical 1D or 2D periodic structures) [19,73]. The reaction speed is tuned by changing the surface area, particle size or thickness of thin film layers and reaction temperatures are also dependent on rate, with higher temperatures reached from faster reactions [54,56,63]. Combustion speeds of thermite mixes are highly varied depending on particle size and surface area. For example, Al/CuO burning rates range from 1 m·s^{−1} to 2200 ± 300 m·s^{−1} for sputtered layers and CuO nanorod/Al nanoparticle mixes, respectively [74,75]. Temperatures reached during reactions also depend on the reactants: thermites can reach thousands of degrees Celsius with rare earth metal reactions, but a more well known mix of 2 Al + Fe₂O₃ can reach up to 3135 K.

With high temperatures and high gas generation from selected thermite mixes, it is possible to find a replacement for primers containing azides, styphnates and other primary explosive compounds normally used in airbags, weapons, explosives and fire extinguishing [3,63,76].

3.3. Semiconductors

Semiconductors are very promising materials for primers due to their electrical conduction characteristics when transitioning from extrinsic to intrinsic majority carrier conduction. Intrinsic conduction typically requires energy (optical, thermal, or electrical by injection current) to be added to the system so that the electrons in the valence (filled) band E_v (Figure 4) can be excited into the conduction band E_c [77]. Doping of Si with impurities such as boron and phosphorus, where the outer electron shell contains 3 electrons (-1 relative to Si) and 5 electrons ($+1$ relative to Si), respectively, allows for current flow at lower system energies, known as extrinsic conduction. This is due to the energy bands of the impurities that are located close to the valence or conduction bands. In Si, boron is an acceptor as it takes an electron from the valence band, producing a hole. Similarly donors such as phosphorus supply an electron to the conduction band as shown in the simple energy band diagram of Figure 4.

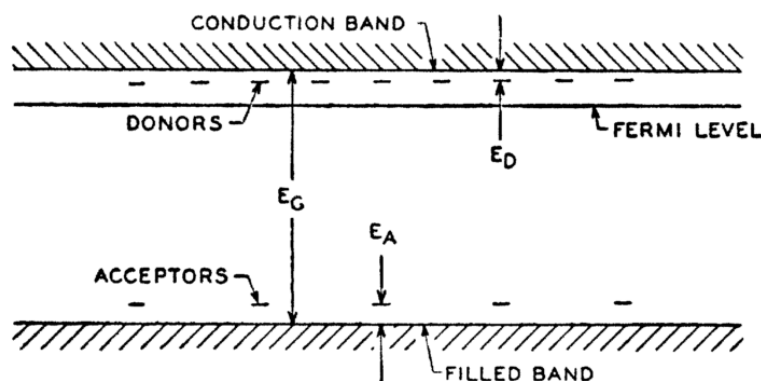


Figure 4. Schematic band diagram for silicon with p-type E_A and n-type E_D dopant energy levels [78].

Silicon-based igniters were proposed in a patent by Hollander, which details the tunability of semiconductors and how they can be used in electro-explosive devices (EEDs). Semiconductor initiators operate on the principle that voltages in excess of threshold V_{th} will produce enough heat to create additional carriers. These will lower the resistance of the device and eventually generate current flow of the intrinsic carriers. Such current flow is a consequence of the negative coefficient of resistance typically exhibited by intrinsic semiconductors [78,79]. Depending on the majority carrier (p- or n-type), the temperature at which intrinsic conduction dominates can be tuned as shown in Figure 5 [78,80,81]. The point at which the majority carrier transitions from extrinsic to intrinsic (degenerate) conduction will determine the temperature at which a large increase in current occurs [82]. At this inflection point, intrinsic carriers start to flow in the conduction band and contribute to ohmic heating. The temperature of the inflection point for Si can be 100–1000 °C, a broad and tunable range. As there is a greater number of intrinsic carriers than extrinsic, the heating rate increases at the transition point and sublimates the material.

The electrical breakdown of intrinsic to highly doped Si into plasma has been demonstrated and fabrication methods are well established, making silicon a candidate for use in initiators [77,83,84]. The ability to tune the temperature of carrier inflection is a beneficial characteristic for matching to the auto-ignition temperature of the next element in the explosive train (typically a propellant like pyrodex) [80].

Silicon can also be fabricated as an energetic material by creating high surface area powders or porous films [85–87]. Porous silicon is created by electrochemical etching and is a highly tunable system for ignition properties and integration into semiconductor based devices [88,89]. Since silicon can be in very different valence states at different oxidation levels, that can be exploited in (photo-)electro-chemical etching methods to deliver different surface morphologies [90]. Surface nano-/micro-roughening can be electrochemically controlled on laser-ablated surfaces of Si [91].

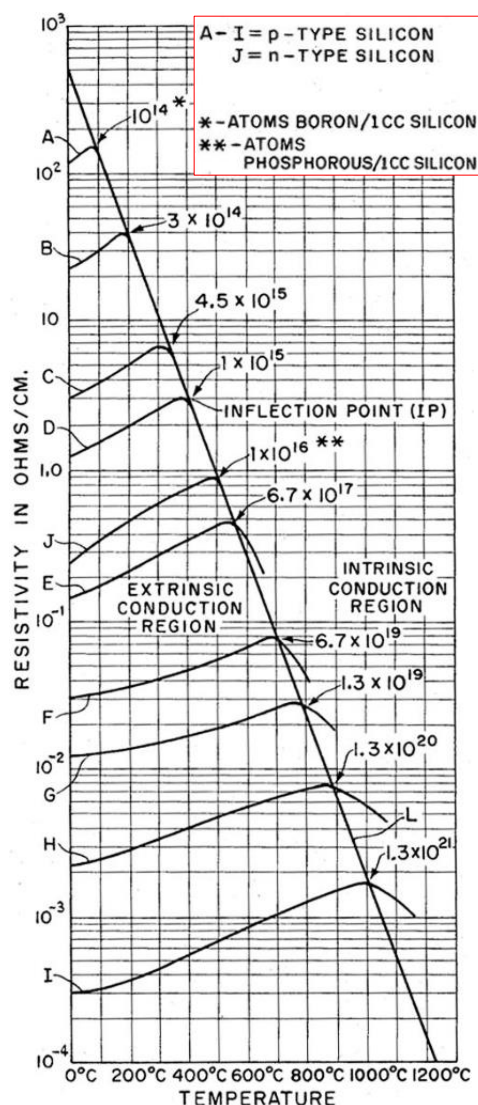


Figure 5. Silicon resistivity at various doping concentrations of boron and phosphorous and its relationship to temperature [80].

4. Ignition Methods

Devices used as primers and initiators contain many components depending on the application and method of ignition. Mechanical initiation is used on percussion caps shown in Figure 2 containing primary explosives [25]. The mechanism of activation requires sufficient impact to compress and shock the priming mix to initiate decomposition. With recent advances from hot-wires to solid-state EEDs, there has been a reduction in initiation energy and activation time for electrically initiated devices [88].

4.1. Electrical

Electrically initiated devices, otherwise known as electro-explosive devices (EEDs), can either use primary explosives that are easily decomposed under electrical discharge, or resistive elements that heat until a reaction or sublimation occurs [92,93]. Electrical initiation is possible by conductive, inductive and electromagnetic signals, provided the input is greater than or equal to the energy required to thermally initiate the device. Thermites and semiconductors can be fabricated for very low electrical initiation energy (millijoules or less) mostly by ohmic heating. Initiation is possible with high current or high voltage, as long as a device-specific threshold value is reached for both parameters. A typical threshold relationship is demonstrated in Figure 6 for a metal bridge wire [93]. As long as the temperature of the material reaches the threshold for a reaction, evaporation, sublimation or electrical breakdown into plasma, the ignition of the device is possible. These EEDs continue to be an area of active interest due to their low initiation energy requirements and short (μs) ignition delays [79,94–96].

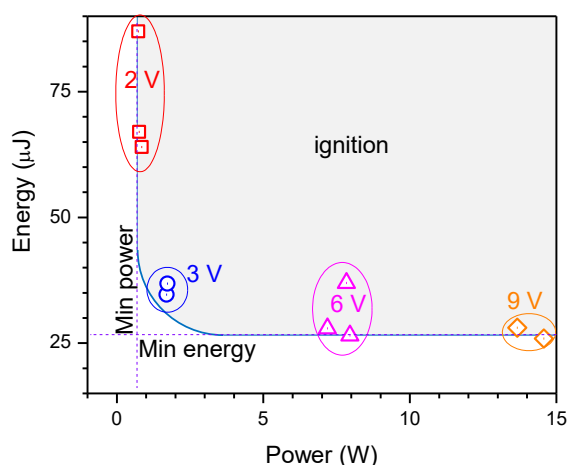


Figure 6. Adapted illustration of the minimum electrical ignition parameters for a $14.5\ \mu\text{m}$ wide metal bridge wire made from layers of 10 nm Cr, 100 nm Ti and 380 nm Au. The minimum power to initiate the bridge is 630 mW and minimum energy is 28 μJ [93].

4.2. Optical

Optical initiation devices can use lasers to ignite explosives and energetic materials [97–100], with the incident light either acting directly on the explosives or on specifically designed light-sensitive devices. Optical initiation typically involves light-induced heating of a substance, whether it be the explosive mix or a light-sensitive compound that transfers the optical energy into another form for ignition [97,99]. High power pulsed lasers have extremely high heating rates, theoretically up to $10^{13}\ \text{K}\cdot\text{s}^{-1}$ while detonation events are reported to be $10^{10}\ \text{K}\cdot\text{s}^{-1}$ [101]. It is preferable for laser ignition of materials to use wavelengths in the visible to infra-red spectrum as diodes operating in that range are relatively inexpensive compared to ultra-violet lasers [102].

The use of high intensity laser irradiation as a thermal initiation method for energetic materials has been widely investigated [32,103]. Lead azide is reported to have a low threshold for laser ignition of $11\ \text{mJ}/\text{cm}^2$ at 1063 nm [104]. In comparison, the safer RDX has been trialed for laser ignition but was found to absorb poorly in the visible-IR and thus needs relatively high power ($>1\ \text{W}$) and long irradiation times ($>60\ \text{s}$) with a 532 nm wavelength. Increasing the absorption of incident light is possible using gold nanoparticles that heat up from the localised surface plasmon resonance effect [102]. Nanoparticle size is tuned to provide optimal absorption at the laser wavelength, causing heat generation

in the nanoparticles and transferring the energy to the energetic material until decomposition occurs. The smaller the nanoparticles, the lower the ignition energy required, with a minimum initiation of 5 W at 808 nm observed for gold nanoparticle doped RDX powder and crystals after a mean delay of 35 and 215 ms respectively. Some interesting energetic materials that are photosensitive but mechanically insensitive are based on carbohydrazides stabilised in graphene oxide [104]. The graphene oxide laminates are reported to provide stabilisation of explosives by reducing sensitivity while also enhancing light absorption.

Ablation with high-peak-power laser pulses provides another method for igniting or detonating materials. A laser pulse of 10 mJ over 8 ns at 532 nm was used to ablate aluminium inside a stoichiometric acetylene-oxygen atmosphere, initiating a detonation from the pressure generated by ablation [105]. Shock wave acceleration is also demonstrated by a laser-supported detonation wave, which involves irradiating plasma from an energetic reaction or explosion to greatly increase pressure in a localised region and enhancing the shock wave propagation [106]. This process requires sufficiently high irradiances of more than $10^6 \text{ W}\cdot\text{cm}^{-2}$ using a 1064 nm 6 ns pulse duration laser with 900 mJ maximum pulse energy. In general, energetic materials were found to have a laser-induced shock velocity of at least $650 \text{ m}\cdot\text{s}^{-1}$, and a close correlation between shock velocity and detonation energy. This also makes the technique useful as a characterisation method for determining energetic material performance.

Optical metamaterials are a fast evolving field that can be connected to initiator applications, specifically via engineered materials with highly tunable properties [107,108]. Perfect absorbers, which have no reflectance $R = 0$ and simultaneously no transmittance $T = 0$ at a specific wavelength, realise perfect absorbance $A = 1$ according to the energy conservation relationship $R + T + A = 1$. Metamaterials rely on nanoparticles of controlled size in arrays/patterns composed of single or layered motifs. For the visible spectral range 400–800 nm, the nanoparticles have to be sub-wavelength and this requires expensive lithographic tools to make them. Layered metal-insulator-metal (MIM) nanoparticles or films can deliver perfect absorbers and this is currently an active field of research for light harvesting and solar cell applications [109]. With the availability of low cost, high optical power $>1 \text{ W}$ light emitting diodes/lasers, perfect absorbers using metamaterials have obvious potential for application in optical primers. The very same principles for engineering light field enhancement and localisation are used for absorption and detection of controlled compounds in the infrared molecular fingerprinting spectral range 2–12 μm [110].

By definition, the initiation by optically induced breakdown occurs when the permittivity $\epsilon = (n + i\kappa)^2$ of a material becomes zero. Here n is the real part of refractive index and κ is the imaginary part. Metamaterials can be engineered to have permittivity (epsilon) near zero (ENZ), which is the state of a material when it strongly absorbs the optically delivered energy. The absorption depth, known as the skin depth l_s , defines the depth of penetration of the light E-field and is given by $1/l_s = \frac{\omega}{c}\kappa$, where ω is the cyclic frequency of light and c its velocity. The pressure as force per unit area [N m^{-2}] is equal to the absorbed energy in the volume [J m^{-3}]. Strongly absorbing materials (or engineered metamaterials) deliver a shallow sub-wavelength optical absorption depth and this is a requirement to reach higher pressures. Nanoscale textured surfaces, which reduce reflectivity, are an obvious strategy to increase the proportion of absorbed light.

There is an important consequence for an optically excited material as it transfers to the ENZ state (also called Die-Met [111] as the dielectric transitions to a metallic state). The absorbed energy density scales as $W_{abs} \propto \frac{n_e}{n_{cr}} F_p \propto F_p^2$ [112], where the excited electron density is proportional to the pulse fluence $n_e \propto F_p$, and n_{cr} is the critical plasma density at which it reflects and is dependent on the wavelength. Even for a single-photon absorption process, which is linear in terms of optical energy (or power, intensity, dose), the absorbed energy density grows as the square (nonlinearly). The design of layered metamaterials which are tailored for ENZ performance at the wavelength of excitation is therefore an interesting strategy. Potential advantages include a lower laser power for stronger optical excitation, no requirement for

complicated nanolithography tools to define nanoparticle arrays, and they can be tailored for specific laser (or LED) wavelengths.

5. Devices

Primers need to be integrated into an end product that contains all of the components for base functionality by electrical or optical initiation. Additional components might include protective elements, booster compounds or pyrotechnics [54,113].

5.1. Safety Mechanisms

Electrical initiators invariably require protective components relating to electrical system vulnerabilities such as electrostatic discharge (ESD) and electromagnetic initiation by radio frequency (RF) signals. The Schottky diode is one component capable of providing protection from ESD, where conduction band height mismatch provides preferential conduction in one direction and opposes current in the reverse direction [114–116]. This reverse bias can prevent conduction up to a threshold voltage depending on the barrier height before reverse breakdown occurs. It is recommended that the Schottky diode barrier height is greater than the initiation voltage of the device so ESD protection is available up until initiation [117]. An example configuration of Schottky diodes is to shunt ESD into a substrate, protecting the device from initiation. This is done by placing the diodes in forward bias to the substrate while in parallel to the device [95].

Protection from RF ignition can be provided with a ferrite bead in series or a capacitor in parallel to the device, as shown in Figure 7. Both are tunable to help dissipate RF energy away from the device for various frequency ranges [118,119].

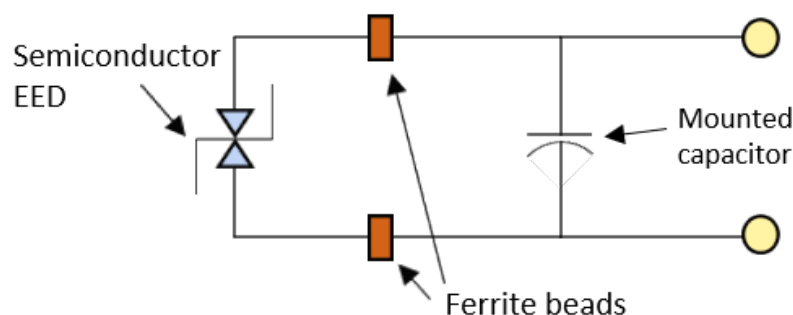


Figure 7. Adapted circuit diagram of an electro-explosive device (EED) with radio-frequency (RF) and electrostatic discharge (ESD) protective elements [118].

5.2. Optimising Output

Optimisation of EED performance is crucial for efficiency of ignition and transfer of energy along the explosive train without loss to the surrounding system. Adding boosting compounds to the base initiator is common. For example, reactive powders containing metals and oxides of various particle sizes can be added to EEDs for increased energy output [19,74,120]. Laminated coatings of Al/MoO₃ or other thermites have also been used to enhance the output energy [56].

A thermally insulating layer underneath the EED reduces heat dissipation into the substrate and thus lowers the required initiation energy. This is demonstrated with an SU-8 resist pillar array fabricated by standard lithography techniques and used to support a membrane of SU-8 with a layer of polyethylene terephthalate (PET) to thermally insulate the device. Next a tungsten filament is deposited onto the SU-8/PET layer as the electrical initiator and then a series of Al/CuO layers are placed on

top. When a current is passed through the tungsten, resistive heating occurs and is unable to dissipate effectively through the SU-8/PET layer. The reduction of thermal energy to transfer into the surrounding environment provides significant reduction in required firing energy, from no fire for currents up to 4 A on a Si substrate, to 100% ignition at >500 mA on a glass substrate and >250 mA on the SU-8/PET layer. There is also a reduction in ignition time, which depends on the input energy and amount of thermal insulation (Figure 8).

The ratio of fuel to oxidiser in a reactive mix plays an important part in the overall energy output during ignition. For CuO and Al nanoparticles, maximum combustion speed was found to be at a fuel:oxide stoichiometry of 1.6:1, which was also observed and preferred for other metal rich reactions, including nanoparticles and thin film multilayers [54,56]. When combustion speeds increase, peak pressure maxima are greater, which makes finer reactive powders or higher surface area mixes ideal for optimising performance [63]. Laser ignition of Al and MoO₃ thermite powders sees a reduction of ignition time with a slightly fuel rich (1.2:1 fuel:oxide stoichiometric ratio) when the Al particles are smaller than a threshold size, which suggests a relationship between theoretical maximum density and ignition performance [121].

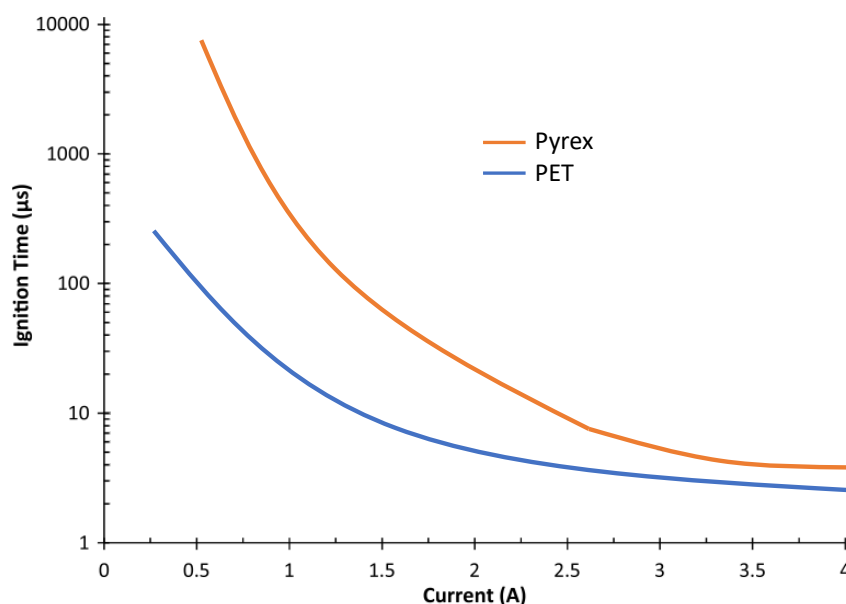


Figure 8. Adapted illustration of firing delay times for initiators on SU-8/PET and Pyrex insulating layers at varying currents [55].

The length and width of the bridge in EEDs affects the firing current, where smaller bridges with higher resistance have lower firing energy thresholds than larger bridges [95]. This bridge area and firing current relationship tends to be linear, as demonstrated in Figure 9 for a Pd bridge, because any proportional increase in length and width will not change resistance, but will alter the minimum required initiation current. The minimum initiation current for a bridge of any material is dependent on the bridge resistance R [Ω] and the voltage V applied, as defined by Ohms law (Equation (1)):

$$R = \frac{\rho L}{A}, \quad V = IR, \quad (1)$$

where ρ is the resistivity of the material [$\Omega \text{ cm}$], L is the length (cm), A is the cross-section area [cm^2] and I is the current [A]. The resistivity is given by:

$$\rho = Ce^{\frac{E_G}{2kT}} \quad (2)$$

where $C \approx 1.1 \times 10^{-4}$ [$\Omega \cdot \text{cm}$] is a constant, k is the Boltzmann constant 8.69×10^{-5} [$\text{eV} \cdot \text{K}^{-1}$], T [K] is the absolute temperature, and E_G [eV] is the bandgap energy. For silicon, $E_G = 1.12$ eV.

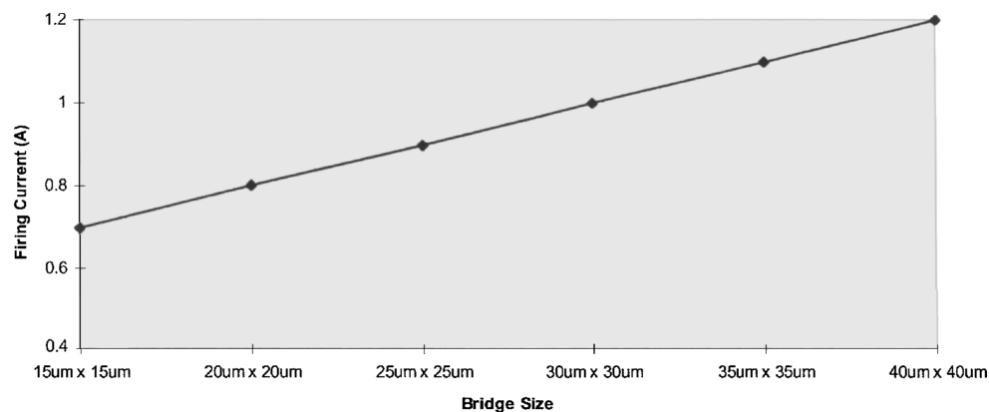


Figure 9. Firing currents for palladium bridges of varying length and width with thickness unchanged [95].

Constraining the flame or shock wave propagation with the use of structural boundaries such as the blasting cap, container housing or shaped walls will increase the energy translation to the next element [1,122]. Called an explosive lens, this is beneficial for constraining the shock wave towards a desired direction and creating a shaped or flat detonation wave for equal impact of the next element in the explosive train [123].

5.3. Testing Standards

A range of manufacturing, performance and testing standards have been developed to ensure that critical products meet requirements for functionality, reliability and interoperability. US Military Standard (US MIL-STD) documents, amongst others, serve as an example for standardisation testing. Electrical initiators would typically undergo various tests according to US MIL-STDs for performance, lifetime, shipping, storage, reliability, stability and calibration before the devices would be considered for use [124,125]. A European patent designed an electrical igniter to operate with all-fire (AF) characteristics of 1.2 A over 2 ms or 1.75 A over 0.5 ms and no-fire (NF) of 0.4 A over 10 s for automobile specifications [126]. AF and NF standard specification requirements can change depending on the application and industry.

Methods of testing devices for their firing parameters is efficiently done using the Neyer D-Optimality test, a method published in 1994 that can efficiently characterise the full distribution and desired quantiles in a population batch of fabricated devices [127]. It is meant to be an improved means of testing a population compared to the Bruceton binary search method. The D-optimality method is used to test the AF and NF characteristics of devices for ensuring high percentile confidence of firing parameters [24,124,128].

The D-optimality test algorithm is able to estimate parameters using a probability response function and a three step process to quickly determine pass and fail parameters in a minimal number of tests. The first step of the algorithm is to use an accelerated binary search within estimations of the upper and lower limits. Once a measured pass and fail is found, another binary search is performed between the lowest success and the highest failure until the difference is less than the estimated standard deviation.

The last step is to refine the pass-fail parameters by binary searching in smaller steps defined by the average of the lowest success and the highest failure and the standard deviation is multiplied by 0.8 for each sample tested. The result is an efficient method for determining parameters in a distribution [127].

5.4. Initiators: Practical Aspects of Fabrication

There are many materials that can be used to produce EEDs including combinations of thermites and semiconductors. The standard convention for EED design includes large electrical contact pads with a narrow bridge connection using any conductive material. The bridge is an intentionally designed fail point with the highest relative electrical resistance and thus selectively localised heating when electrically loaded. The resulting shape of devices are typically very similar and conventionally called a bow tie [95].

A reactive metal-based device consisting of a Pd layer with a bow tie shape and a Zr cap over the bridge portion is shown in Figure 10 as an example of an EED igniter [95]. Electrical initiation is performed by sending a current across the device and resistive heating of the Pd causes the temperature to rise enough for evaporation and ionisation of the metals, producing a plasma. The Pd bridge dimensions are adjusted to control the resistance across the junction and Zr is deposited as a reactive metal coating to produce hot particles alongside the plasma when electrically fired. The Schottky diodes formed by the Al/Si junctions shown schematically in the side view of Figure 10 provide a shunting mechanism for any possible ESD. The resulting shape of the bow tie device provides a contact pad area and a localised ignition point in a simple design [18,24,56,88,129–133].

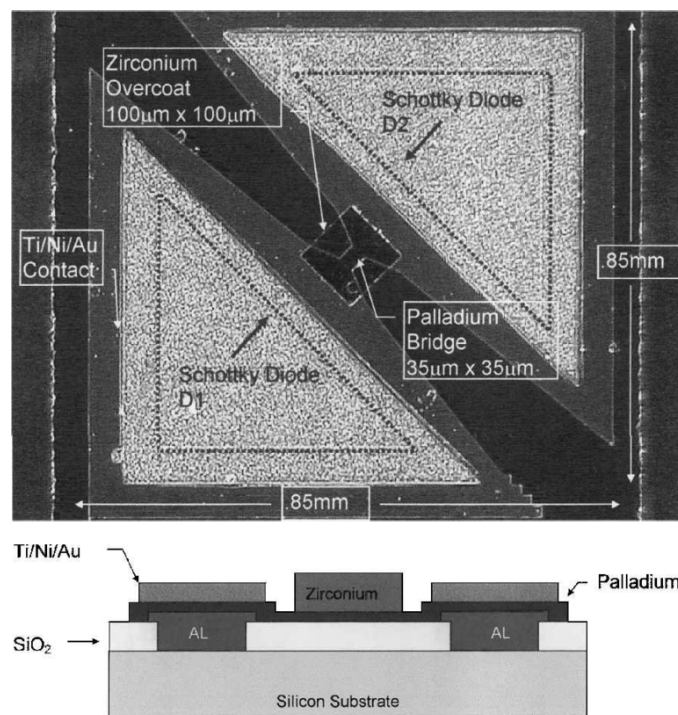


Figure 10. Top view of a palladium and zirconium bow tie electric initiator and side view schematic of the final device with Schottky diode [95].

An EED using a thermal oxidation process in a furnace to create CuO nanowires over the bridge is shown in Figure 11 [134]. The bridge is shaped as a square zig-zag and the Cu is coated over the top. When Cu is heated at 450 °C in a furnace and exposed to oxygen, nanowire crystals of CuO will form in a two stage oxidation process: Cu to Cu₂O to CuO [135]. After the oxidation of Cu, Al is thermally evaporated on

top and a high surface area thermite is created. Because Cu can be electroplated, thick films are fabricated at a much faster rate than vacuum-based deposition. The thermite mix can easily be electrically isolated using thin films of insulating materials, but can still be initiated from the bridge underneath when required. Patented devices also identify tungsten (W) as a bridge material for EEDs due to the low ignition energy and shorter initiation times compared to standard metal bridges [136].

A semiconductor bridge (SCB) initiator made of $100 \times 380 \times 2 \mu\text{m}$ ($L \times W \times T$) polysilicon doped with phosphorus at a concentration of $\sim 7 \times 10^{19} \text{ cm}^{-3}$ has been fabricated on sapphire (SOS) or silicon-on-insulator (SOI) substrates [96]. Aluminium lands are connected to the sides of the bridge as electrical contacts (Figure 12) and also act as Schottky diodes. Upon application of sufficient energy, the bridge vaporises and produces a plasma which provides a low resistance conduction pathway. The production of plasma occurs within a few μs and is referred to as the late time discharge (LTD) phase of firing. The approximate energy required to reach LTD is equal to the heat of sublimation of the material, provided that minimal heat is lost to the surrounding environment.

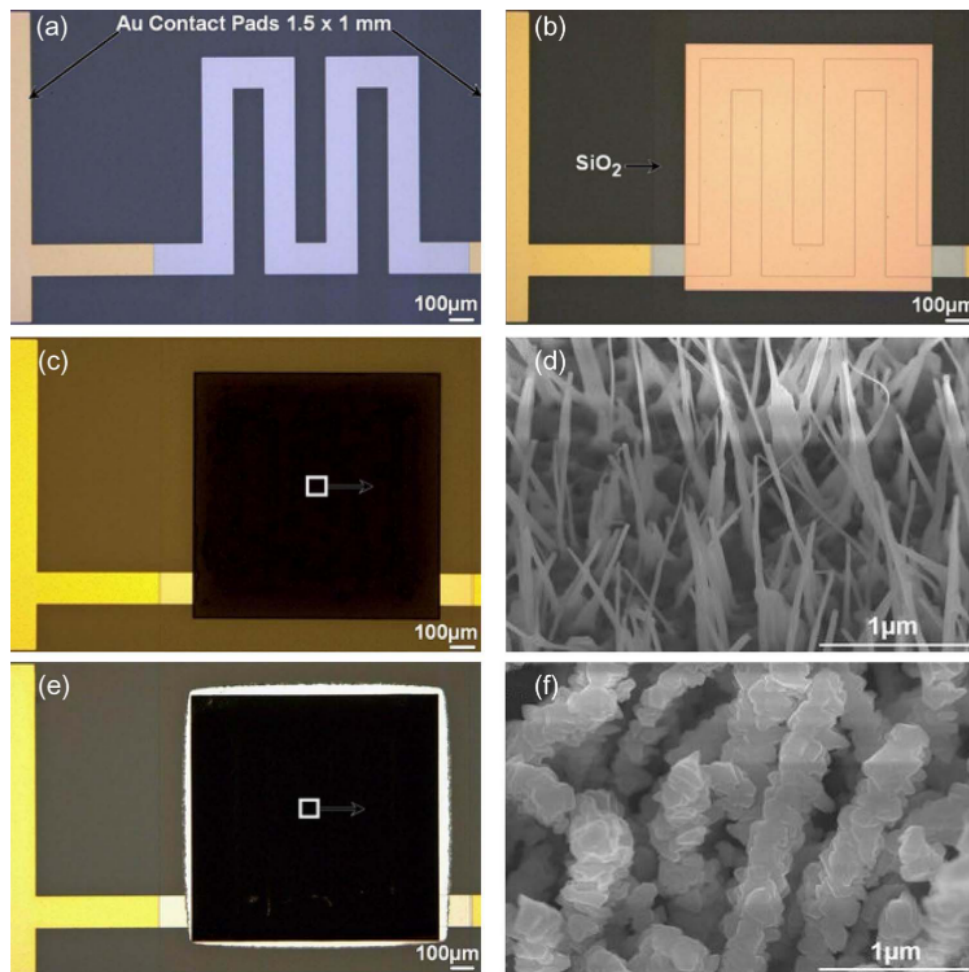


Figure 11. Optical images of (a) Au/Pt/Cr EED bridge; (b) SiO_2 and Cr coating over the bridge; (c) CuO nanowires; (d) SEM image of CuO nanowires, similarly for (e,f) with a thermally evaporated Al coating [134].

The late time discharge of EEDs is important for energy transfer to the next constituent of the device, e.g., black powder propellant. It is important that enough material is available in the device

to be consumed in the LTD to provide energy transfer onto the propellant. Ignition of various compounds has been reported, including titanium sub-hydride potassium perchlorate ($\text{TiH}_{1.65}\text{KClO}_4$), PETN, 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX), pentaamine(5-cyano-2H-tetrazolato-N₂) cobalt(III) perchlorate (CP) and lead azide, but we are not aware of a black powder DDT by only the electrical initiator [96,137].

Firing of the EED requires sufficient electrical energy to ensure transition of the device from solid to plasma. The bridge resistance in a bow tie configuration (Figure 10) is around $1\text{--}2\ \Omega$ as a compromise between ease of firing and prevention of activation from standardised ESD tests [96,124].

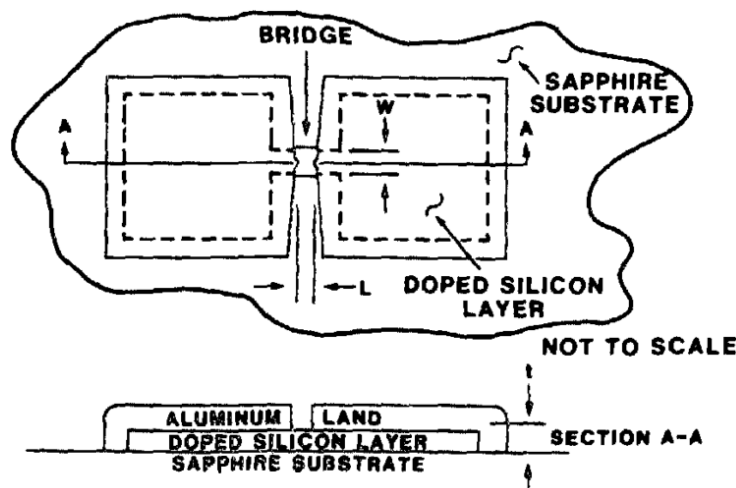


Figure 12. Silicon SCB top and side view schematics [96].

Laser initiated igniters can operate to directly ignite an energetic compound or use a sacrificial metal layer to absorb the laser energy, termed a laser explosive bridge wire. Laser initiated devices are generally simpler in design than electrically initiated devices, only needing an optical window for transparency of the incident laser light to initiate the primer compound [32]. Optical igniters offer advantages over electrical igniters as they do not need any complex manufacturing steps or protective ESD and RF elements, but the laser diode electronics are still susceptible to ESD. Instead the primer compound and laser wavelength need to be carefully selected depending on the application. PETN powder of $1\text{--}2\ \mu\text{m}$ was found to have significantly lowered initiation energy for 1064 and 532 nm laser wavelengths using 0.1–0.2 % concentration by mass of 100 nm aluminium nanoparticles [138].

6. Characterisation: Techniques and Principles

Energetic material performance can be described initially by detonation velocity, detonation pressure and heat of explosion [52]. These are the first characteristics that should be looked into for primers when determining performance. Some of these parameters are listed in Table 1 and have been derived from various test methods. The Trauzl lead-block test measures the deformation induced by 10 g of explosive in a standardised lead block as a means to compare performance [139,140].

High speed camera photography is used frequently to image burn and propagation rate, size of emitted particles or ionised gas, and ignition delay (also measured by oscilloscope) [56,141]. Figure 13 shows snap shots of a typical plasma formation sequence after application of a 420 V bias to a metallic bridge. The ignited bridge creates a plasma that expands during discharge and the plasma arc simultaneously consumes the electrode pads.

Shockwave generation and velocity have found interesting characterisation methods using bubble generation in water, interferometry with a split beam and schlieren imaging during ignition [142–145]. Pressure sensors and optical fibres in pressure tubes or chambers can also measure gas generation and shockwave velocity by spacing the measurement points along the length of the tube in increments away from the igniter [75]. Piezoelectric sensors are small and can be placed in close proximity to optically induced initiators as demonstrated by detecting the acoustic signature of an electron plasma formed in glass [146].

The plasma electron density of EEDs has been measured in vacuum using a microwave resonator probe. Electron density is dependent on material, mass and power input with a logarithmic decay of density with increasing distance from the igniter [147]. Differential scanning calorimetry (DSC) on reactive materials can provide very useful information such as heat of reaction and phase transition temperatures [86,92].

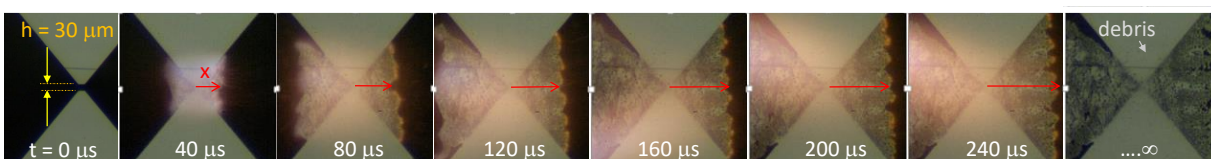


Figure 13. Temporal evolution (t) of an electrically driven plasma plume (420 V bias) with lateral cross-section $2x$. Imaging of the plasma plume was performed at $25\text{k frames}\cdot\text{s}^{-1}$ (Phantom CineMag II v711, Vision Research Ltd, operated with a proprietary zoom lens from CSIRO). The bridge was $30\text{ }\mu\text{m}$ wide, $30\text{ }\mu\text{m}$ long and formed by micro-layers of Ti/SiO₂; resistance of the bridge was $R = 261\text{ }\Omega$.

Non-contact optical methods to characterise chemical composition and temporal evolution of explosions based on light emission are well developed. The associated spectroscopic instrumentation is relatively simple and can also be portable. The slope of the dependence of light intensity plotted as $\log(\text{Intensity} \times \lambda^2)$ vs. $h\nu$ allows the black body temperature to be estimated, where $h\nu$ is the photon energy and λ is the corresponding wavelength [148].

For the analysis and modeling of shock wave propagation, the scale-invariance and self-similarity of the explosion provides a predictive tool. It is based on hydrodynamic scaling laws that allow the comparison of explosions occurring on very different time and length scales, as was demonstrated for an optically induced micro-explosion [149]. The velocity v_0 and time t_0 of the explosion are related to the deposited (or optically absorbed) energy E_0 , which is related to generated pressure P_0 and mass density of the environment ρ_0 :

$$v_0 = \sqrt{P_0/\rho_0}; \quad t_0 = \sqrt{R_0^5 \rho_0/E_0}. \quad (3)$$

If the shock wave velocity v_0 is measured, e.g., by shadowgraphy, the pressure at the shock wave front directly follows from Equation (3) as $P_{sh} = v_0^2 \rho$.

Therefore the density of the material is a very important factor and enters the design of primers when oxidation reactions and surface areas of powdered/granular explosives have to be optimised for efficient shock compression. Void formation inside sapphire ($\rho_0 \approx 4\text{ g}\cdot\text{cm}^{-3}$) induced by a tightly focused $\lambda = 800\text{ nm}$ wavelength and $\sim 150\text{ fs}$ laser pulse of only $E_0 = 100\text{ nJ}$ (absorbed energy) is comparable with an underground (similar ρ) nuclear explosion of $E_0 = 25$ kilotons energy (TNT equivalent) in terms of the deposited energy density $P_0 = 1.2 \times 10^7\text{ J}\cdot\text{cm}^{-3}$ or 12 TPa [150]. The optical pulse is focused close to the diffraction limit of $R_0 \approx \lambda/2$ and the hydrodynamic movement of material starts after electron energy is coupled to the ions in plasma, hence $t_0 \approx 4\text{ ps}$. This is the time of the microscopic explosion t_0 , while the macroscopic explosion takes $\sim 50\text{ }\mu\text{s}$ and starts from a volume with a cross section of $R_0 = 2\text{ m}$. In both

cases the velocities reach strong shock conditions with $v_0 \sim 50 \text{ km}\cdot\text{s}^{-1}$, which far exceeds the speed of sound in the surrounding material ($\sim 10 \text{ km}\cdot\text{s}^{-1}$ for sapphire). This example shows the extraordinary range over which micro-explosion dynamics scale: a small energy of 100 nJ in a very small volume with sub-micrometer cross sections creates the same extreme conditions as a macro-scale event [150]. Hydrodynamic scaling is an indispensable tool for the design and modeling of early stage prototypes of optical primers.

7. Conclusions and Outlook

The development of solid-state primers has typically included the use of thermites, reactive metals and semiconductors as the main constituents or mixes in EED fabrication. These EEDs are most commonly made via deposition techniques and can generate enough energy and heat to initiate the propellant. However, the majority of reported explosives ignited have been used in tandem with a booster compound. One such compound, $\text{TiH}_{1.65}\text{KClO}_4$, has been used to avoid the primary explosives and heavy metal compounds traditionally used as primers in explosive devices. A simple, commonly used design consists of a bow tie shape where a tunable restricted channel, known as the bridge, connects two larger electrical contact pads. This has the benefit of increased resistance relative to the rest of the device, which promotes localised thermal heating and provides a novel means of electrical activation. Although the performance of EEDs do not match that of the compounds they are replacing, knowledge of DDT processes and the addition of booster compounds has supported the development of near industry-ready igniters.

The use of metamaterials and perfect absorbers in optical primers is the next frontier for achieving safer, non-contact ignition with light sources. Various protective elements can be added to explosive devices and their performance can be controlled better using electrical and optical initiation methods. It is expected that new principles of initiation will be developed first for a specific application and then will widen their field of use. Historically this practice has been observed in a range of industries, including primers.

Most importantly, we can expect that by transferring to new methods of electrical and optical initiation in the explosive train (or in some part of it), future solutions will become non-toxic, less susceptible to malfunction and expand into wider use in modern technologies. Although some of the emerging principles of implementation are at a very early stage of development, optical technologies are advancing rapidly in this “century of light”. For example, via the Indirect Fire Protection Capability, the defence technology sector is pursuing laser gun prototypes aiming at 300 kW power, which was an insurmountable challenge just a few years ago [151].

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