Direct bonding CVD-grown diamond to ZnSe and sapphire

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Abstract: We report plasma-assisted direct bonding of CVD-grown diamond to ZnSe and sapphire. Bond survival is demonstrated from -40 to 80°C, while localized heating of the diamond/ZnSe bond showed exceptional heatspreading performance.

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1. Introduction

Diamond is proving an increasingly important material in optical and electronic devices due to its excellent non-linear, mechanical and thermal properties. Diamond's unrivalled thermal conductivity ($>1500 W m^{-1} K^{-1}$@300K) [1] is over 50 times greater than that of sapphire ($27 W m^{-1} K^{-1}$) [2] , making it an ideal material for heatspreading. In addition, diamond's hardness renders it extremely resistant to wear or indentation damage, offering an appealing structural support for more fragile materials.

Zinc selenide (ZnSe) has been demonstrated as an excellent host medium in mid-infrared laser operation when doped with chromium or iron [3]. In contrast to diamond, ZnSe suffers from an extremely low mechanical hardness and has a significantly lower thermal conductivity ($18 W m^{-1} K^{-1}$@298K) [2], combined with a high thermo-optical coefficient ($\frac{dn}{dt}$), leading to detrimental effects when power-scaling. Combination of the two materials is therefore of interest for engineered media, allowing diamond to compliment ZnSe's optical properties through improved thermal management and mechanical protection. Moreover, the close refractive indices of each material make waveguide structures an appealing prospect. The thin-disk architecture is another promising approach for power-scaling [4], where the heatspreading potential of diamond would provide exceptional performance. However, the mid-infrared absorption of diamond is incompatible in the case that the diamond were intra-cavity. As such, the design would require direct bonding of diamond to a suitable terminating layer (such as Al_2O_3) of a high-reflectance dielectric mirror coating between the thin-disk and heat spreading diamond layer.

Joining of diamond and ZnSe presents some difficulties due to the notable difference in their respective Coefficients of Thermal Expansion (CTE), which limit elevated temperature procedures. In this work, combination of diamond to ZnSe is achieved at room temperature, using a plasma-assisted direct bond to produce a void-free, optically lossless and thermally conductive interface. In addition, diamond to sapphire bonding is conducted via the same technique. To demonstrate the bond's potential for heatspreading in an active waveguide, durability over a range of temperatures and ramp rates was investigated. A localized heating test, via an optical pumping scheme, demonstrated that for a bonded ZnSe/diamond interface, the thermal lens strength was diminished by at least two orders of magnitude compared to the bare substrate alone.

2. Direct Bonding

Direct bonding relies on intimate contact between surfaces. In most cases, a nanometer-scale separation must be achieved in order to facilitate successful bonding, requiring stringent polishing and cleaning routines. ZnSe and sapphire faces to be bonded were polished to an RMS roughness $<$1nm. However, achieving an equivalent surface finish on diamond is a difficult prospect, reflected in a poorer recorded RMS roughness of $\approx$2nm. Fortunately, this is counteracted by a greater Hamaker constant, increasing the van der Waals force produced during bonding. Therefore, provided an appropriate activation was conducted, the diamond surface quality was found suitable for bonding.

Cleaning, activation and bonding were conducted in a class 1000 clean room facility. Prior to bonding, samples were cleaned through a multi-stage, ultrasonic treatment in solvents and de-ionised (DI) water. Following this, a two-stage oxygen and nitrogen plasma clean was conducted, developing a hydrophilic surface state. Diamond and ZnSe, both

Fig. 1. 500μm thick diamond bonded to 4mm thick ZnSe and also to 660μm thick sapphire wafers.

naturally inert and hydrophobic materials, demonstrated natural contact angles of 40° and 70°, respectively. Following plasma activation, these were reduced to less than 5° on both materials.

Nitrogen plasma has been demonstrated [5] to encourage a hydrophilic state by bombarding faces to be bonded, leaving dangling bonds of high surface energy. Following activation, bonding faces were brought together via DI Water at room temperature and produced spontaneous contact. Bonded samples were then left under pressure for at least 24 hours. Fig. 1 shows ⍉5mm CVD-grown diamond samples bonded to ZnSe & sapphire. Inspection of the ZnSe-diamond bond revealed a clear interface with two small air gaps visible toward the bond edge. The bonding process was confirmed by successfully conducting two further diamond to ZnSe bonds in the same manner. For sapphire bonding, a diced segment of 0.67μm thick sapphire wafer was used as a substrate material. Successful contact was achieved over half of the bond area, displaying a clear interface.

3. Temperature Trials

A series of trials were conducted to test the composite's resistance to temperature change and ramp rates. First, heating was applied via a hot plate, increasing to 80°C in 5°C increments. The temperature was measured by a thermocouple placed close to the diamond on the ZnSe surface. No change was observed up to 55°C, at which point the bond was noted to shrink slightly away from the edges. By 80°C an unbonded ring was clearly visible around the central bond, as shown in Fig. 2 (A). Sharp, dark-lined edges developed around the remaining bonded area, forming a hard barrier to further delamination at the bond edge. These lines were inspected using a microscope and white light interferometer and found to be locations where the ZnSe surface had dislocated, distorting the bulk substrate to maintain contact with the diamond, as shown in Fig. 2 (B) and (C). The composite was then held at 80°C for eight hours to test durability. No further degradation was noted. Cooling to room temperature also saw no change to the bonded region, beyond softening of the sharp bond edge lines. Further increase of temperature to 150°C saw the loss of all clarity in the bond. Failure of the bond then occurred during cleaning with acetone at room temperature.

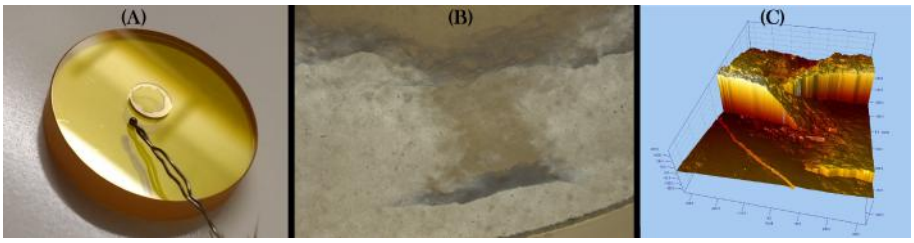

Fig. 2. (A) The diamond/ZnSe composite at 80°C, (B) a 10x microscope inspection of the failed bond region and (C) A 3D surface map of the ZnSe surface following bond separation.

A second diamond/ZnSe composite was ramped to 80°C at rates of 1, 2, 5 and 10°C/minute. As before, the bond shrank at the outer edges, but no further damage was observed, demonstrating resistance to sharp changes in environmental temperature. Afterwards, the bond was cooled over a liquid nitrogen bath on a metal frame. A nitrogen flow was maintained over the sample to stop condensation forming and restrict the rate of cooling. A minimum temperature of -40°C was recorded, and the bond was held between -20 and -15°C for 10 minutes. Minor degradation at the bond edge was observed, mirroring the changes witnessed with increasing temperature, apart from the development of hard edges to the bonded region.

4. Localised Heating Trial

To investigate the heat spreading benefits of the diamond/ZnSe composite, a localized heating comparison was made with bare ZnSe. A 445nm diode was collimated with a lens (L1), f=8mm, before focussing by a second lens (L2), f=25mm, to an approximately 30x140μm radius waist near the ZnSe surface. A 1064nm laser beam was directed through the rear ZnSe face to overlap with the 445nm beam on the front face. The beam was focussed by a lens (L3), f=200mm, to a radius of 140μm. The reflection off this face was captured by a lens (L4), f=150mm and focused onto a Spiricon CCD positioned at the Fourier plane of the lens, as shown in Fig. 3(A). The 445nm beam waist was positioned just within the sample's surface, adjusted to the position of maximum thermal lens for the bare ZnSe surface.

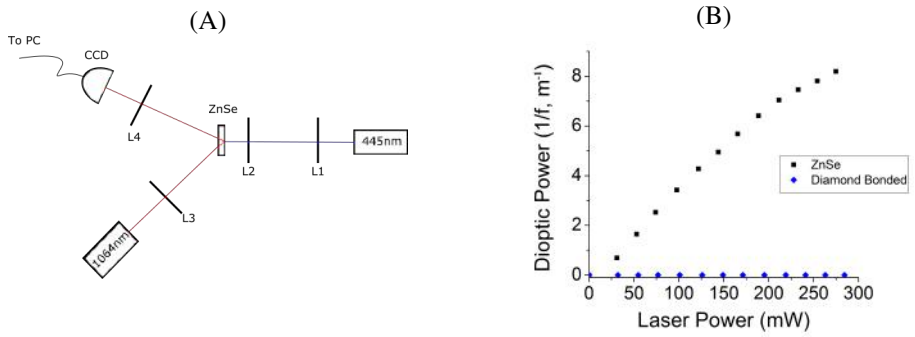

Fig. 3. (A) Pump-probe setup design to compare thermal lensing in bonded and unbonded ZnSe and (B) optical power of induced thermal lens with increasing laser power.

The power of the 445nm pump was increased to 300mW while the probe beam diameter was recorded at the CCD, then compared with a bonded area covered by the 500μm thick diamond layer. A maximum thermal lens dioptic power of 8.2m^{-1} was observed for the bare ZnSe. When scanned within the diamond bonded region, no thermal lens was detected within the limits of our setup (to 0.3% resolution). Fig. 3 (B) shows the optical power (in diopters) of the thermal lens detected for both regions tested.

5. Summary

We have successfully bonded CVD-grown diamond to zinc selenide and sapphire using plasma activated bonding. Despite their CTE difference, the bond is resistant to temperature changes over -40 to 80°C. When compared to bare ZnSe, a localized heating trial of the composite demonstrates exceptional heat spreading as the observed thermal lens was reduced by at least two orders of magnitude in our experimental setup. Several engineered optical structures based on diamond/ZnSe composites can be envisaged for both active and passive devices using this direct bonding technique.

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