CVD DIAMOND FOR NEXT-LEVEL PERFORMANCE IN SEMICONDUCTOR APPLICATIONS

INTRODUCTION

The combination of ever-decreasing feature sizes and increasing power requirements places extreme demands on the physical and electrical properties of the materials used in advanced semiconductor devices. Consequently, there is a significant research effort ongoing for the development of new, more robust materials that can be used in such devices. As well, quantum computing research needs new materials that enable long spin-state coherence times and operation at or near room temperature. Diamond has the potential to satisfy the material needs of these devices.

Diamond is an allotrope of carbon with the same crystal structure as silicon. Its material properties are remarkable; it exhibits the highest room-temperature thermal conductivity (Table 1, Ref. [1]), it is the stiffest and least compressible material, it has high optical transparency from the UV through to the infrared regions of the spectrum, and it is chemically and biochemically inert (Table 1, Figure 1a).

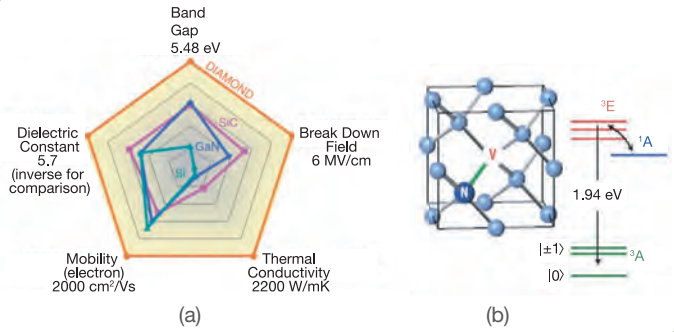

Figure 1 - (a) Electrical and thermal properties of diamond vs. other semiconductor materials [22]; (b) the NV vacancy center in diamond [3].

Undoped diamond is an electrical insulator with a higher dielectric breakdown strength than, for example, silicon dioxide. P- or n-doped diamond has semiconducting properties that surpass those of silicon and the alternative materials currently used in advanced devices. Nitrogen-doped diamond (NV diamond) has nitrogen-vacancy color centers that exhibit spin coherence times up to hundreds of microseconds at room temperature (Figure 1b, [2] [3]).

Electrical and Thermal Properties	Si	SiC-4H	GaN	Diamond
Band Gap (eV)	1.1	3.2	3.44	5.5
Breakdown Field (MV/cm)	0.3	3	5	20
Electron Mobility (cm^2/V-s)	1,450	900	440	4,500
Hole Mobility (cm^2/V-s)	480	120	200	3,800
Thermal Conductivity (W/cm-K)	1.45	3.7	2.53	22.9
Thermal Expansion Coefficient ($10^{-6}K^{-1}$)	2.3	2.8	3.2	1
Baliga's Figure of Merit*	1	290	910	17,200

**Baliga's Figure of Merit (BFOM) is defined as: $BFOM = \varepsilon\mu E_G^3 \cong {V_{max}^2}/{R_{on}A}$ where ε, μ, E_G, V_{max}, and $R_{on}A$ are the dielectric constant, carrier mobility, bandgap energy, breakdown voltage, and specific on-resistance, respectively [5].*

Table 1 - A comparison of the electrical and thermal properties of some advanced materials for device fabrication [1].

Such long spin-state coherence can facilitate the development of room-temperature quantum computing. Diamond is also a preferred material for use in certain MEMS applications and its high dielectric strength makes it suitable for use in semiconductor devices operating in medium-to high-power regimes [4] [1], including in some advanced Schottky diodes. Its use in a variety of other semiconductor device applications (e.g. as a heat sinks and spreaders, especially for High Electron Mobility Transistors (HEMTs) is currently being investigated ([2] and references therein).

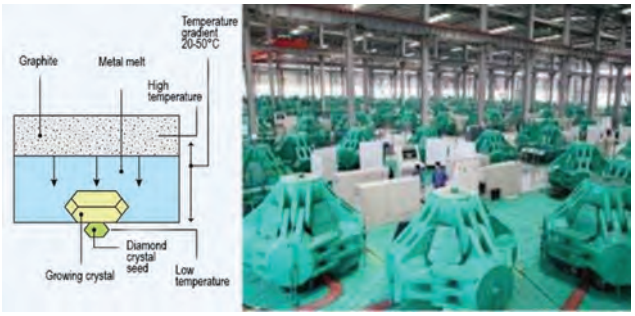

Figure 2 - HPHT Process: a) schematic; b) equipment.

"Artificial" Diamonds by High-Pressure High Temperature Processes

The synthesis of "artificial" diamond has a long history. High-Pressure High-Temperature (HPHT) methods for production of both gem-quality and "industrial diamonds" were initially developed in the 1950s. These processes (Figure 2) use extremely high temperatures and pressures to transform sp^2 carbon materials such as graphite to sp^3 diamond. Direct conversion of graphite to polycrystalline diamond by HPHT is typically carried out at pressures > 10 GPa and temperatures > 2000°C (Figure 2, Figure 3). The use of metal-carbon alloys as a carbon source mitigates these conditions to pressures of 5 - 6 GPa and temperatures of 1300 - 1600°C. Within the process, the metal melt dissolves carbon from a graphite source, transferring it through solution to a seed crystal where a diamond film slowly grows on the surface. The melt maintains low carbon concentrations that support slow ordered, single crystal growth as opposed to the more rapid polycrystalline growth that would occur at high carbon availability. Table 2 shows the different properties of polycrystalline vs. single crystal diamond films. Diamonds grown by HPHT processes most often exhibit [10] and [11] crystal facets, although process variations in pressure, temperature, and melt composition can yield diamonds having crystal facets with other Miller indices. The size of diamonds grown by HPHT typically range between 1- and 7-mm in diameter with a maximum weight of about 17 ct. These processes can produce both gem-quality stones and polycrystalline industrial diamonds, depending on the process conditions.

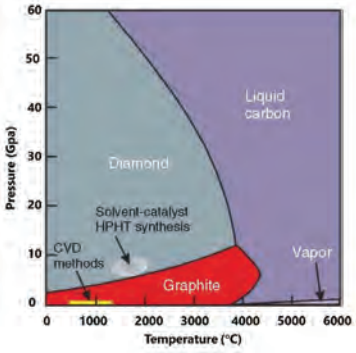

Figure 3 - Graphite/diamond phase diagram [16].

	Polycrystalline Diamond (PCD)	Single Crystal Diamond (SCD)
Structure	Composed of many small diamond crystals	Uniform, continuous crystal lattice
Grain Boundaries	Present, can scatter phonons and electrons	Absent, leading to superior properties
Thermal Conductivity	High, but lower than SCD due to grain boundaries	Extremely high, ideal for heat dissipation
Optical Transparency	Lower, due to scattering at grain boundaries	High, suitable for optical applications
Mechanical Strength	Very hard, excellent wear resistance	Hard and tough, but more prone to cleavage
Applications	Cutting tools, wear-resistant coatings	Quantum devices, optics, high-power electronics
Cost	Lower, easier to produce	Higher, complex and slower growth process

Table 2 - Polycrystalline vs. single crystal diamond properties.

Type	I			II	
	IaA	IaB	Ib	IIa	IIb
[N] (ppm)	> 1	-	-	< 1	-
N Center	A	B	C	-	-
[B]	Low	Low	Low	Low	Dominant
Electrical Resistance	Very high	Very high	Very high	Very high	Low
Color	-	-	Yellow		Blue

Table 3 - Classification of diamond.

Commercial diamond growers employ proprietary melts with mixtures of different elements added to the primary metal species to produce the desired properties in the diamond product. Industrial diamonds produced in high-volume HPHT processes are used in many applications including coatings for cutting and machining tools and as material for use in optical polishing.

While metal contamination in the growing diamond is minimal owing to low solubility in the bulk diamond, light elements such as H, B, or N can easily be incorporated into the crystal lattice. Control of the concentration of these latter contaminants can be used to produce different diamond qualities for different applications (Table 3). N-containing crystals (Type I in Table 3) form point defects or defect clusters (depending upon the N concentration). This produces a change in color in the diamond as well as a high number of dislocations and stacking faults. Defect levels in Type IIa diamond are kept low by increasing the growth rate using higher process pressure.

Selected Diamond Applications

Type IIa clear crystals with low B and low N content are used in both high-end jewelry and industrial/technical application such as wear-resistant coatings. They exhibit exceptional brilliance and clarity, making them sought-after in jewelry as lab-grown ethical and sustainable alternatives to natural diamonds. Technical applications of a Type IIa diamond include optics and windows in laser applications, semiconductor substrates, components in power and high-frequency electronics, and coatings for high-precision cutting tools. While pure diamond is an insulator, doped diamond (Type IIb) crystals have semiconducting properties and are suitable for electronic device applications. Diamonds used in p-type semiconductor applications typically have boron concentrations 10^{15}-10^{19}/cm^2 with a total defect density of < 10^3/cm^2. N-type semiconducting diamond is more difficult to achieve than p-type. This is due, in part, to greater difficulty in substituting a phosphorus atom, which is roughly 40% larger than a carbon atom, into the diamond lattice. This issue has made it difficult to produce n-type diamond for use in p-n junctions, resulting in most diamond-based diodes being p-type Schottky diodes. Table 4 shows the properties of some representative diamond Schottky diodes. Diamond field effect transistors (FETs) for high power applications have been successfully demonstrated but remain largely in research and early commercial development stages. Current reviews discussing diamond FETs are available [6] [7].

Ref.	Diode Type	Substrate	Schottky Electrode Diameter (µm)	Forward Current (A/cm^2)	Rectification Ratio	Breakdown Voltage (V)
[9]	Lateral Schottky	$Ir/SrTiO_3/Si(001)$	180 (Pt)	10	10^{12}	52 (1 MV/cm)
[10]	Lateral Schottky	3C-SiC/Si(001)	50 (Mo)	-1	10^{6}	-
[11]	Lateral Schottky	$Ir/ SrTiO_3/Si(001)$	200 (Zr/Pt/Au)	-10^{-3}	10^{4} - 10^{5}	-
[12]	Lateral Schottky	Al_2O_3 (1120)	100 (Al)	-6	10^{6}	50 (1.1 MV/cm)
[13]	Lateral Schottky	Commercial Product	(Mo/Au)	5×10^{-5}	~10^{6}	375

Table 4 - Electrical properties of heteroepitaxial diamond lateral Schottky diodes [8].

The unique purity and structure of diamond is also being explored for use in quantum technology devices. The properties of NV vacancies in Type Ib diamond are under evaluation as qubits for quantum computing and for use in high-sensitivity magnetic field sensors. As shown in Figure 1b, nitrogen, with nearly (95%) the same atomic radius as carbon, easily substitutes into the diamond carbon lattice to produce an NV (Nitrogen – Vacancy) pair. Electrons trapped in the vacancy can carry quantum information that can be used in quantum computing applications. The spin states of this electron can be read as output by using optically detected magnetic resonance (ODMR). The properties of NV defects are such that, whatever ground-state spin exists in the electron(s) in an NV defect or assemblage of defects, when the diamond crystal is illuminated with green light, statistics favor the electron's spin entering the ms = 0 state. When the crystal is cycled through the illumination loop enough times, the electron spins associated with the NV defects will all be effectively aligned in the ms = 0 state. When this condition is achieved, the ground state of electron in the NV defect can be manipulated and read by applying microwave radiation and additional light pulses.

Epitaxial Diamond by Microwave Plasma Chemical Vapor Deposition Processes

The diamonds produced in HPHT processes have too many defects to allow their use in electronic applications. They can, however, be used as seed crystals for Microwave Plasma Chemical Vapor Deposition (MPCVD) of epitaxial diamond films. Epitaxy, derived from the Greek root words epi, meaning "above", and taxis, meaning "in ordered manner", is defined as the natural or artificial growth of an ordered and oriented crystalline overlayer on a crystalline substrate in which the orientation of the substrate determines the orientation of the overlayer. In the case of diamond epitaxial growth, two different modes of epitaxy are possible: homoepitaxy and heteroepitaxy. MPCVD methods can be used to deposit both homo- and hetero-epitaxial films of single crystal diamond for many applications [14] [15] [16] [17]. Figure 4 shows a schematic of a typical CVD diamond process and equipment.

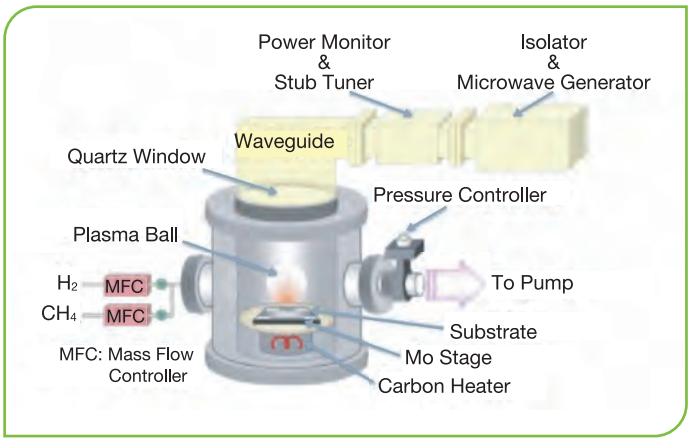

Figure 4 - A typical CVD diamond process set-up.

Homoepitaxial diamond forms new layers of diamond on the surface of a single crystal diamond seed. The homoepitaxial diamond layers form with a crystal lattice orientation that is identical to that of the seed layer. Homoepitaxy produces the purest form of diamond and

it is typically used in gem and tool industry applications. Size limitations in homoepitaxy processes and crystal defects in the product make homoepitaxial diamond films unsuitable for semiconductor applications. This paper will therefore focus on heteroepitaxial diamond processes and applications.

Heteroepitaxial diamond forms new layers of crystalline diamond on a seed layer of crystalline material other than diamond. Heteroepitaxial diamond layers currently have three primary applications: a) as thermal management layers in medium and high power electronic devices, laser diodes, radar amplifiers, and HEMT devices [2] [18] [19]; b) the production of diamond wafers for use as substrates for e.g., devices such as diodes and switches; and c) to produce diamond wafers for use in the formation of quantum computing devices.

Substrates for Heteroepitaxial Diamond

The choice of substrate to produce heteroepitaxial diamond is critical since the surface of the substrate determines the crystalline quality of the resultant film. Important parameters for substrate selection include the crystal structure, the lattice constant of the surface facet, and the thermal expansion coefficient of the substrate relative to that of diamond. As well, the substrate surface must be stable to plasma exposure in processes such as MPCVD diamond.

While a wide variety of materials have been evaluated as substrates for heteroepitaxial diamond formation, the preferred material has been determined to be iridium, Ir. The crystallinity of heteroepitaxial diamond on Ir surfaces is an order of magnitude better than that produced on any other substrate. Recently, large, low-cost multilayer substrates have been developed and successfully employed for diamond heteroepitaxy. These substrates have a surface buffer layer of epitaxial Ir (deposited by, for example, e-beam evaporation) on metal oxide-on-silicon structures such as, e.g., $SrTiO_3$/Si and YSZ/Si, and, more recently, on sapphire/Si and $KTaO_3$/Si.

Heteroepitaxial Diamond by MPCVD Bias Enhanced Nucleation

MPCVD processes employ a gas feed containing a carbon source (e.g., methane, CH_4) and hydrogen (H_2) in a ratio of, typically, 1:99. The gas is fed into a process vacuum chamber containing a heated substrate on which the diamond film is grown. MPCVD processes may be used for both homoepitaxy and heteroepitaxy and can produce thin films for device components or thick films suitable for use as semiconductor substrates (Figure 5).

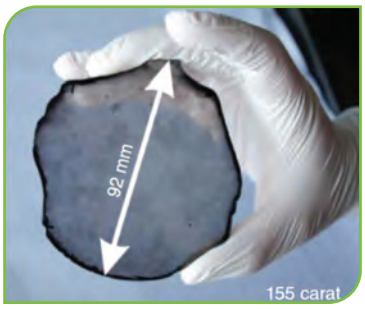

Figure 5 - A diamond substrate produced by MPCVD [21].

MPCVD diamond process pressures range between 20 and 400 mbar and substrate temperatures may vary between 300 and 1200°C, depending on whether polycrystalline or epitaxial diamond films are targeted. The gases are excited using microwave radiation to create a plasma that contains reactive ions and radicals. Microwave excitation at 2.450 GHz is used for small growth areas, while excitation at 915 MHz is used for larger substrates. Microwave powers of 3 - 5 kW are employed in plasma generation. $C_xH_y^{\bullet}$ radicals are generated in the gas phase and these diffuse to and adsorb on the growing diamond surface (Figure 6). Hydrogen radicals from the gas phase both etch away more reactive sp^2 carbon surface species

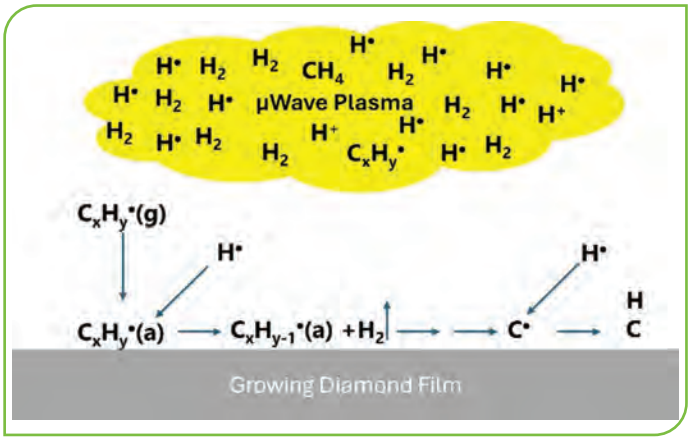

Figure 6 - MPCVD of diamond from CH_4/H_2 mixtures.

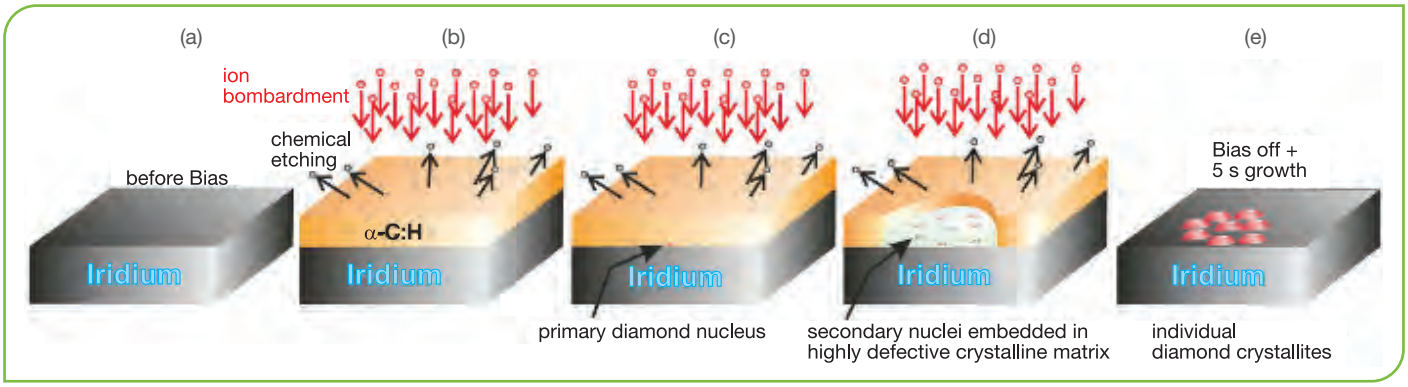

Figure 7 - BEN on Ir. a) pristine Ir surface exposed to plasma before biasing; b) an amorphous C:H layer immediately forms at the beginning of the BEN process. Equilibrium between deposition and etching by atomic hydrogen limits layer thickness to a constant value of 1 - 2 nm; c) spontaneous formation of a primary diamond nucleus; d) lateral expansion of the domain and formation of secondary nuclei embedded in highly defective α-C:H matrix; e) during the first 5 seconds after termination of BEN, atomic hydrogen completely etches the α-C:H phase with the formation of crystalline diamond grains having a height of 2 nm at a distance of 15 - 20 nm [21] [8].

and ensure that sp^3 carbon at the diamond surface is H-terminated, preventing rearrangement back to the lower energy sp^2 carbon. Hydrogen radicals also abstract hydrogen from H-terminated carbon at the diamond surface, creating dangling bonds that act as high energy sites for the further adsorption of reactive gas-phase CxHy• radicals, continuing the growth of the diamond film (Figure 6). Volatile dopant sources can be added to the gas feed in MPCVD to produce semiconducting doped diamond films (diborane, B_2H_6, or trimethylboron, $B(CH_3)_3$, for P-doped diamond and phosphine, PH_3, for n-doping). Under optimized conditions, deposition areas appropriate to semiconductor wafer processes (10 - 20 cm diameter, Figure 5) can be achieved. Growth rates of greater than 10 µm/hr have been realized with dislocation densities of $< 10^7/cm^2$.

The application of a negative bias to the substrate at the beginning of the MPCVD process produces ion bombardment of the growing surface. This Bias Enhanced Nucleation (BEN) of diamond films was first developed by Yugo et al in 1991 [20] and it has become the most successful means of producing heteroepitaxial diamond films on a variety of substrates, including iridium. During the initial ion bombardment phase of BEN, diamond formation competes with both surface roughening and the formation of an amorphous C:H (α-C:H) layer on the Ir surface. According to Schreck, diamond nucleation occurs via a mechanism they labelled as Ion Bombardment-Induced Buried Lateral Growth (IBI-BLG) [21] [8]. According to this mechanism (Figure 7), the α-C:H layer forms as soon as bias is switched on. This α-C:H layer remains during ion bombardment, in an equilibrium between deposition and removal by atomic hydrogen. It is limited to an equilibrium thickness of 1 - 2 nm (Figure 7b). During the initial ion bombardment phase, diamond nucleation occurs at the α-C:H/Ir interface (Figure 7c). These nuclei undergo lateral growth to form an extremely thin and highly defective 2D layer of crystalline diamond (Figure 7d). When the bias is switched off, atomic hydrogen completely etches away the α-C:H layer, leaving the diamond nuclei on the Ir surface to act as seeds for the MPCVD heteroepitaxial process (Figure 7e). Under appropriate MPCVD conditions and without bias, a fully epitaxial diamond layer grows, as shown in Figure 8. The crystalline diamond produced in the fourth growth phase shown in Figure 8 typically has a minimal dislocation density of approximately $10^7/cm^2$.

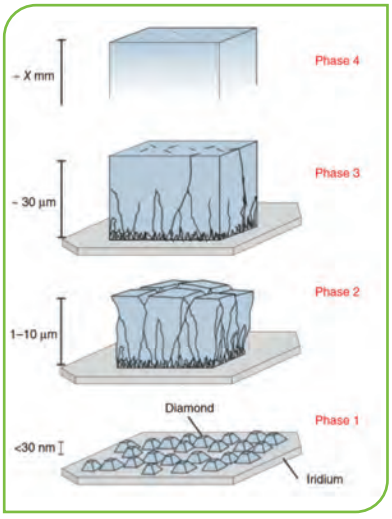

Figure 8 - The stages of growth of epitaxial diamond on an Ir substrate.

SOLUTION

MKS offers the Alter® 915 MHz GS Series and the Alter® 2450 MHz industrial microwave generators for use in MPCVD diamond processes (Figure 9).

The Alter 915 MHz GS Series generators provide 15 to 100 kW of microwave power, depending on the model. Power is delivered from a shielded cabinet with continuous powerline control, safety interlocks, various interface options, and optional remote control. The Alter 2450 MHz generators are designed as rugged and reliable switch mode power supplies for demanding industrial applications. These are compact generators that deliver up to 15 kW of microwave power in a 19-inch standard rack with a remote head and integrated isolator. All MKS microwave generators are equipped with switch mode topology for all power ranges and support a variety of fieldbus communications protocols.

CONCLUSION

Ever-decreasing feature sizes and increased power requirements are combining to make CVD diamond substrates more important for semiconductor device development. The exceptional thermal properties, chemical stability, and wide bandgap of diamond make it the best choice as both a substrate and component material in many advanced device designs. These properties enable efficient heat dissipation, high-power operation, and enhanced performance in devices such as high-frequency transistors, laser diodes, and quantum components.

Microwave plasma CVD diamond can be deposited with precise purity and thickness, making it ideal for advanced microelectronics and photonics. Microwave generators create the plasma environment that produces highly reactive ionic and radical hydrogen and carbon species that accomplish diamond epitaxy in the process. MPCVD can produce either single-crystal or polycrystalline diamond films in pure or doped forms that can be tailored for individual semiconductor applications.

As device miniaturization and power density increase, the demand for materials that can handle extreme thermal and electrical conditions grows. MPCVD diamond is emerging as a strategic solution for next-generation semiconductor devices, including those used in quantum computing, RF electronics, and high-voltage power systems.

Figure 9 - MKS Alter® industrial microwave generators. a) 915 MHz; b) 2450 MHz.

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