CHAPTER 2

THEORETICAL BACKGROUND

This chapter begins with the review of plasma state and the introduction of low temperature plasma. Then, the system generated low temperature plasma, radio frequency inductively coupled plasma (RF-ICP) will be described. Finally, the fundamental processes in plasma and the effect of plasma on textile will be described.

2.1 Definition of Plasma

Plasma is so called the fourth state of matter [18]. The first state is solid and it is the coldest state of matter. When solid is heated up, it becomes liquid which is the second state of matter. When liquid is heated up, the liquid turns to gas which is the third state of matter. And when gas is heated up, atoms break apart in to charge particles turning the gas into plasma. Fig. 2.1 shows the four states of mater as temperature increases. However, any ionized gas cannot be called a plasma. A definition of plasma is a quasineutral gas of charged and neutral particles which exhibits collective behavior [19].

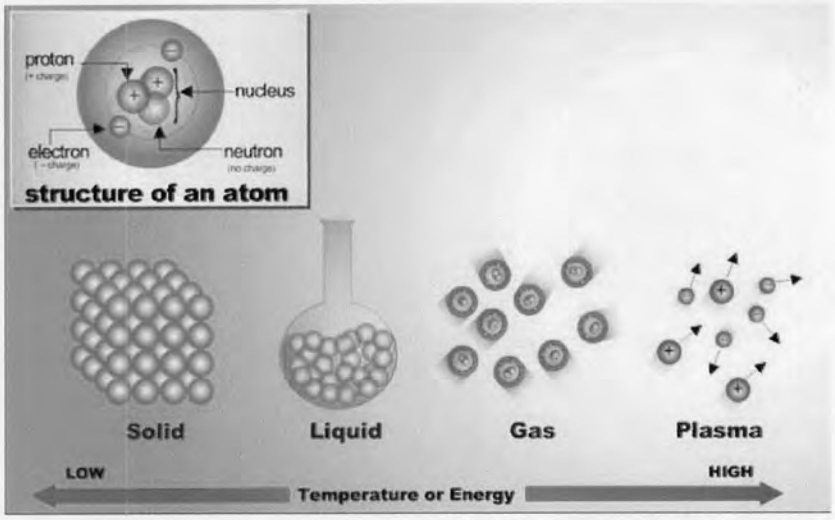

Figure 2.1: The four states of matter versus temperature [20].

2.2 Type of Plasma

The plasma state exists in the universe or is created under characteristic situations for particular purposes. The plasmas form in the nature cover a very large range of electron densities and gas temperatures which can be classified into two types; (a) local thermodynamic equilibrium plasma and (b) non-local thermodynamic equilibrium plasma.

2.2.1 Local thermodynamic equilibrium plasma

Local thermodynamic equilibrium (LTE) plasma is also called high temperature or hot plasma. It is mostly created in star. For LTE plasma, the electron temperature (T_e) is nearly equal to gas temperature (T_g) which temperature in the rage of 10^6-10^8 K (10^2-10^4 eV) [21]. However, this type of plasma is only idealistic significance since it can not be created in the laboratory environments.

2.2.2 Non-local thermodynamic equilibrium plasma

Non-local thermodynamic equilibrium (non-LTE) plasma is also called low temperature or cold plasma. The low temperature plasma is produced under low pressure system (pressure less than several tens Torr). Due to the gas pressure is low (large mean free path), the collision frequency between electrons and gas molecules becomes small. As the result, the gas mainly consists of neutral rather than excited species. A characteristic of this type of plasma is the absence of thermal equilibrium between the electron temperature and the gas temperature. For low temperature plasma, the electron temperature is much higher than the gas temperature ($T_e \gg T_g$) [21]. The electron temperature can reach tens of thousands of K, while the gas temperature is only hundreds of K (room temperature).

There are several systems that can produce low temperature plasma such as direct current (DC), alternating current (AC), a high frequency (HF) including radio frequency (RF) or microwave (MW). In this thesis, the RF is chosen as power source. The detail of system producing low temperature plasma will be described in section 2.3.

2.3 Radio Frequency Inductively Coupled Plasma

Radio frequency inductively coupled plasma (RF-ICP) is one type of discharge which transferred energy to plasma by electromagnetic induction. Because RF-ICP system produces uniformly plasma and high plasma density (10^{10}-10^{12}cm^{-3})[22], therefore it has important advantages in applications for material processing.

2.3.1 The component of RF-ICP system

Simplified schematic diagram of the RF-ICP reactor is shown in Fig. 2.2, it can be divided into three main parts as the following;

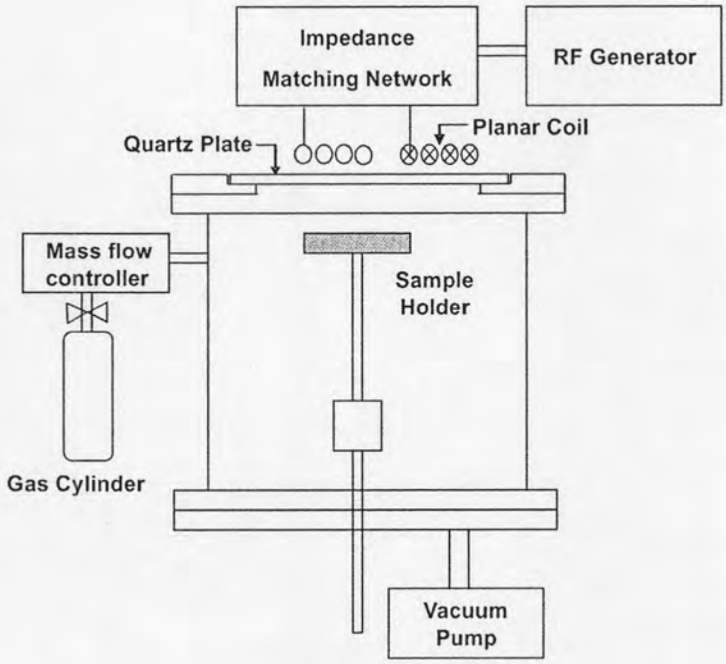

Figure 2.2: Diagram of the radio-frequency (RF) inductively coupled plasma reactor.

1) Gas flow system consists of the gas cylinder and the flow rate controller. The flow rate of gas is controlled by a mass flow controller.

2) The vacuum system consists of the vacuum chamber and the vacuum pump. Typically, the reactor chamber is made of stainless steel rather than quartz tube because it is easy to alter the body of chamber in order to apply several ports for diagnostic.

3) The RF power coupling module consists of the RF generator, induction coil (planar coil), which is placed at center and above the quartz plate, and impedance matching network. The impedance matching network use to match the source's output (RF generator impedance of 50Ω) into the load impedance of the discharge (plasma impedance approximately of 1Ω). The impedance matching network is based on LC resonant circuit which consists of a network capacitor and inductor. Several configurations of this device, such as L-type, π-type, and T-type depend on the arrangements of capacitors and the inductors [23]. In this thesis,

the π-type network is used because it is more efficient than the other configurations [23].

2.3.2 The energy transfer of ICP system

When RF generator forwards RF current and transfers to the planar coil, a time dependent magnetic field *H(r,t)* will be generated and induces a time dependent electrical field *E(r,t)* according to the Faraday's law,

$$\vec{\nabla} \times \vec{E} = -\mu_0 \frac{\partial \vec{H}}{\partial t}, \tag{2.1}$$

where μ_0 is the permeability of free speace. In the case of planar coil, can be described using cylindrical coordinate $(\hat{r}, \hat{\theta}, \hat{z})$, where $\hat{r}$ axis is in a radial direction of the planar coil, $\hat{\theta}$ axis is in an azimutal direction, $\hat{z}$ axis is perpendicular to the planar coil. The generated magnetic field has two components H_r and H_z ($B = \mu_0 H$) around the planar coil, while the induced electrical field is in azimutal direction (E_θ). The RF magnetic and electrical line are presented in Fig. 2.3.

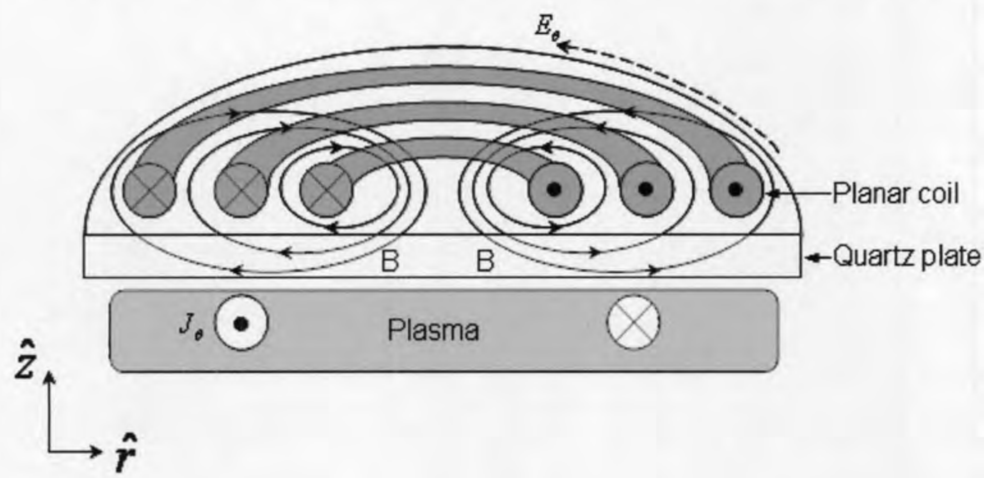

Figure 2.3: Shows RF magnetic and electrical field lines [24].

The electrical field accelerating electrons move in a closed annular path. The moving electrons collide with gas molecules or heavy particles within the reactor chamber, producing ion, electron and neutral species. The collision process is described in section 2.4. Through collision process, the plasma can be occurred. When the plasma occurs underneath the planar coil, the generated magnetic field in the planar coil induces electrical field E_θ and current density J_θ in the plasma according to the Ampere's law

$$\vec{\nabla} \times \vec{H} = -\epsilon_0 \frac{\partial \vec{E}}{\partial t} + \vec{J}, \tag{2.2}$$

where ϵ_0 is permitivity of free space. The occurring current in the plasma is in the opposite direction to the current which rotate in the planar coil. They behave as air-core transformer [24]. Here, the RF power planar coil is the first turn of the transformer and the plasma is the second turn. For this reason, Inductively Coupled Plasma can be also called Transformer Coupled Plasma (TCP) [22].

2.4 Fundamental Process in Plasma

In the plasma, there are charged species (electrons and ions) and neutral species (gas atoms and molecules). The chemical reaction within the plasma is resulted from collision process between these particles and can be classified into two types; (a) reaction of electrons with heavy species occurring by inelastic collisions (exchange of internal energy) between electron and heavy species, (b) reaction between heavy species. However, in low temperature plasma the reaction between the electron and the heavy particle are dominate [21]. So, in this thesis, we will describe only reaction of electron with heavy species.

When electrons with sufficient energy from applied external electromagnetic field resulted in electrons collide with gas molecule and transfer its energy to gas molecule. These collisions lead to various reactions in the plasma. The important process can be presented as the following;

Ionization. The primary electron impacts with gas molecule (represented as A_2) producing positive, atomic, or molecular ion and two electrons which can produce further ionization to sustain the plasma.

$$e^- + A_2 \rightarrow A_2^+ + 2e^-. \tag{2.3}$$

Recombination. It is the reverse process of ionization reaction. An electron combines with the positive particle, resulting positive particle disappears from plasma.

$$e^- + A^+ \rightarrow A. \tag{2.4}$$

Excitation. The incoming electron has not enough energy to ionize atom, but it has enough energy to excited electron in ground state to excited state.

$$e^- + A_2 \rightarrow A_2^* + e^-. \tag{2.5}$$

Relaxation. This process immediately occurs after excitation process. The excited electron can stay in excited state very shot time period and then it return to a lower energy level or ground state at the same time, emitting a photon (ν), as well known electromagnetic radiation.

$$A_2^* \rightarrow A_2 + \nu. \tag{2.6}$$

Dissociation. An electron collides with gas molecule, resulting the molecule is dissociated without formation of ions.

$$e^- + A_2 \rightarrow A + A + e^-. \tag{2.7}$$

Attachment. This process can occur, when electronegative gas is used. An electron collides with a gas molecule (represented as AB), the electron is captured by the gas molecule. So, the molecule becomes a negative ion.

$$e^- + AB \rightarrow A + B^-. \tag{2.8}$$

Detachment. It is the reverse process of attachment reaction. A negative ion releases an electron, forming neutral gas molecule.

$$A + B^- \rightarrow AB + e^-. \tag{2.9}$$

2.5 Reactions Between Plasmas and Textile Surfaces

Generally, the plasmas consists of free electrons, several different ions, radical, photons (ν) and a lot of different excited particles depended on the used gas. The reactive species in the plasma can interact with textile surfaces and change their chemical and physical properties. The reactions between plasmas and textiles can be classified as follows;

1) Surface reactions: they are related to both reactions between surface species and the reactions between gas-phase species and surface species which produce grafting and functional groups, respectively, at the surface. Example of gases that can produce these reactions are carbon dioxide, ammonia, hydrogen, nitrogen, oxygen and fluorine etc. [1, 25].

2) Plasma polymerization: it is a process for material surfaces modification by deposition of organic polymer film under the influence of plasma. Example of organic gases and vapors that can produce polymer via polymerization are C_2H_6, CF_4, C_3F_6 or C_2F_4 [1, 10].

3) Plasma etching: it is a process which materials on surface are removed by bombarding of energetic particles in the plasma. Chloride or fluorine containing plasma and oxygen plasma can produce etching process [1, 7].

As mentioned earlier, fluorine-containing plasma can produce all of reactions (surface reactions, plasma polymerization, and plasma etching), however, the reactions prodominate will depend on the type of fluorine-base gas feed, the operating plasma conditions, and the chemical nature of the textile [10, 25, 26].