Instructions for use

Solvent effects in the transient characteristics of liquid-gate field effect transistors with silicon substrate

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Abstract

The transient characteristics of EDL-gated field effect transistors with Si as an active semiconductor were studied using various electrolyte solutions of $LiBF_4$ by applying a step-function voltage in order to determine the optimum electrolyte for semiconductor circuits using EDL. The t_R, determined by EDL dynamics in the present experiment, showed a minimum as a function of the solvent due to the competing effects of the EDL thickness and viscosity. The t_R of the electrolyte solutions with various solvents at the same concentration were classified into three categories: slow response of a complex-forming solvent, medium response of protic solvents and fast response of nonprotic solvents. The best response time was 55 μs when a 1.0 M acetonitrile solution was used as the liquid-gate insulator.

1. Introduction

Ion dynamics in electric double layers (EDLs) is very important for the application of EDLs in energy storage devices and electronics. An EDL field effect transistor (EDL-FET) is an application of EDLs, which takes advantage of nm-size thickness of the EDLs[1-13]. It uses the electric field at the semiconductor - electrolyte interface to control the carrier concentration in the semiconductor by changing the "gate bias voltage" applied to the counter electrode. The field effect at a constant bias voltage becomes greater if the capacitance of the gate is greater. In this sense the EDL-FET has an advantage over the conventional FET using solid insulators. The characteristics of the EDL-FETs include a very high carrier accumulation in semiconductors with a relatively low gate bias voltage[1-4,7]. The study of EDL-FETs was initiated in 1980s [1-3] and it is now gathering much attention on the physics of very high carrier density in semiconductors[10] and practical device application to low mobility materials, such as organic semiconductors[4-9], to reduce the power consumption. EDL-FETs will find further applications because the liquid EDL will fit many morphologies. In principle, semiconductor nanoparticles, fibers, and even compressed powders can be used as transistors with EDL gates, which will lead to printable semiconductors from inorganic materials.

In practical application to the printable electronic devices, the switching speed of EDL-FET is very important. It is naturally considered that the long response time (t_R) of an EDL might be a disadvantage for using EDL-FETs for practical electronics. The t_R of the EDL must be evaluated and the optimum conditions to minimize the t_R should be studied. This kind of information will also be beneficial for the application of EDL capacitors. The dynamics of EDL-FETs with a polymer

electrolyte has been studied as a drain current transient[3] as well as the transient characteristics of EDL capacitors[14,15], which was interpreted as a result of a simple capacitance-resistance (CR) product. Accordingly, the frequency response of liquid electrolytes has been studied using a capacitance analyzer[4,11,14]. However, it is not evident whether a simple CR circuit is generally sufficient for the analysis because there are two different species, i.e., anions and cations, responding differently to the electric field. In particular, their response in solutions with a low viscosity can be different from polymer electrolytes, in which the ionic motion can be coupled with the fluid dynamics response.

The purpose of the present study is to clarify the EDL dynamics by measuring the transient response of the EDL-FETs. This experiment will answer the above-mentioned questions because ionic motion dynamics at the interface can be evaluated as the transient of the drain current in the EDL-FETs. Si is used as an active semiconductor because its mobility is high enough to investigate the response of the EDLs not limited by the carrier dynamics in the semiconductor. The transient characteristics of the EDL capacitors were first analyzed to confirm the necessity of a detailed analysis. Next, the t_R of the EDL-FETs with various electrolyte concentrations was studied and then the effects of the viscosity and the chemical nature of the solvent-ion interaction were also investigated.

2. Experimental Procedures

The EDL capacitors were fabricated as follows. Silicon wafers with a thermal oxide layer (700 nm) (SiO_2/Si) were used as the substrate. A SiO_2/Si wafer was cut into 13 × 13 mm^2 squares, and then 100-nm thick aluminum was vacuum deposited on the SiO_2/Si. A glass cylinder with a 4.5-mm inner diameter was glued on the Al/SiO_2/Si using epoxy resin.

We employed LiBF$_4$ as the ionic source and changed the solvent. We also tried to use C$_6$H$_{11}$N$_2$ BF$_4$ and (C$_4$H$_9$)$_4$N BF$_4$ in addition to LiBF$_4$ but found that LiBF$_4$ showed the fastest response. In addition, the solubility of LiBF$_4$ was by far highest to many kinds of solvents. We aimed to see the response at very high concentration where the effect of concentration and viscosity competes, and the solvent effects in detail, and therefore we focus on the result of LiBF$_4$ electrolyte in this paper.

After a LiBF$_4$ electrolyte solution was added to the cylinder, a cylinder-shaped aluminum counter electrode with 4.2 mm diameter was immersed in the electrolyte. The distance between the counter electrode and the substrate was changed between 0.2mm to 3mm but it did not make difference to the measured transient characteristics.

The silicon EDL-FETs were fabricated as follows. High resistivity (1000 - 3000 Ωcm) silicon wafers (thickness 380 μm) were cut into 13 × 13 mm^2 squares and cleaned by the RCA method[16] to remove all metal contaminants and particles. Subsequently, the Si wafers were immersed in a diluted HF solution to remove the oxide layer[16]. A high resistivity of the Si was very important in order to observe its FET characteristics, in other words, a low drain current when V_G = 0 can be achieved using highly resistive Si.

The aluminum source and drain electrodes were vacuum deposited as soon as possible after the HF treatment. A glass cylinder similar to the one previously described was glued on the substrate using epoxy resin including the channel region between the source and the drain electrodes. After a LiBF$_4$ electrolyte solution, which is considered to be a liquid gate, was added to the cylinder, a platinum gate electrode with a sufficiently large surface area was immersed in the electrolyte. The setup to the measure the drain current transients of the EDL-FETs is illustrated in Fig. 1.

Gradual degradation of the transistor performance was observed when the applied voltage difference between electrodes (Pt wire, drain and source) was larger than 0.9 V. We postulated that this was due to the oxidization of the Si surface. The obtained results were free from degradation and the effects of the atomic order oxidization of Si surface should be negligible as long as the response time is the only important parameter to be determined.

3. Results and discussion

We first evaluated the transient response of the EDL capacitors. Dots in Fig. 2 show the current transients of the EDL capacitors for various $LiBF_4$ concentration in N,N-dimethylformamide (DMF) when a voltage ($V = 750$ mV) was suddenly applied at time $t = 0$ μs. It was found that the response cannot be fitted by a simple exponential function, which corresponds to a current transient ($I(t)$) of a CR series circuit that is given as $I(t)=(V/R)\exp(-t/CR)$ [13]. Instead, we found that at least three exponentials, $I(t)=\sum_{i=1 \text{ to } 3} a_i \exp(-(t-t_0)/t_i)$, in which t_0, a_i and t_i are fitting parameters, are necessary for the fitting as shown in Fig. 2. The time constants (t_i) obtained from the fitting are summarized in Table1. Since the distance between the electrodes did not affect the transient response, we consider that the resistance of the bulk electrolyte is not relevant to it. We noticed that hunching is observed in Fig. 2. We have carefully examined the measurement circuit but the amplitude of the hunching was not controllable. It might come from the measurement circuitry or from some fluid mechanical oscillation while the EDL capacitors were being charged.

The t_R of the EDL-FETs was measured as a function of the $LiBF_4$ concentration for the DMF solution. To evaluate the t_R of the EDL-FETs, the following experimental technique was used [17]. When a step-function gate bias was applied, the current through drain was measured by an oscilloscope. The settling time of the applied step-

function voltage to measure the drain current transient was approximately 4 μs, which was fast enough to investigate the transient characteristics of the EDL-FETs. The current through drain showed a sudden increase as shown in Figs. 3(a) and 3(b) when the step-function gate bias was applied. This sudden increase was caused by a displacement current when the EDL-gate capacitor was being charged. When a drain voltage (V_D) was applied (V_D= -0.5 V), the current through drain (I_D') had two components, which were a drain current (I_D) and a displacement current (I_d), i.e., I_D' = $I_D + I_d$. The component of the displacement current must be removed to evaluate the correct t_R of the EDL-FETs. The component consisting only of the displacement current can be measured by measuring the current through drain when $V_D = 0$ V. Therefore, I_D can be calculated by subtracting I_d from I_D' ($I_D = I_D' - I_d$).

Figures 3(c)-3(e) show the response of the drain currents determined by the above method. Figures 3(c)-3(e) all represent the response of the EDL-FETs using the liquid electrolyte gate of DMF solutions containing $LiBF_4$ at different concentration. They are well fit by a single exponential function using formula $I_D(t) = I_{D0} - \Delta I_D \exp(-t/t_R)$, where $I_D(t)$ is the drain current as a function of time, I_{D0} is the steady-state drain current, ΔI_D is a constant, and t_R is the relaxation time constant. The obtained t_R values are summarized in Table 1. The t_R decreases as the concentration of the electrolyte solution increases from 0.010 M to 1.0 M. These t_R values reflect the ion dynamics at the Si/electrolyte solution interface because the mobility of Si is not very low that might limit the frequency response.

It is easily noticed that the characteristic time constants (t_1, t_2, t_3) obtained from the fitting of the EDL capacitors and t_R values from the EDL-FETs are not directly related. The probable reason is that the transient response of the EDL capacitors is complicated because the motions of the anions, cations, and bulk electrolyte are involved. The fitting by three exponential functions cannot separate the contribution of each motion.

This result indicates that the measurement of the transient response of the EDL-FETs is important in order to evaluate the ionic motion at the interface.

It is thus important to measure the relationship of the t_R with the concentration and the electrolyte solvents. The t_R values of the EDL-FETs were measured as a function of the LiBF$_4$ concentration for the various kinds of solvents. It was expected that the response of EDL-FETs strongly depends on the electrolyte concentration. The relation between the viscosity of the electrolyte solutions and the t_R was investigated since the viscosity is an important parameter to determine the t_R. Viscosity values of 7 different electrolyte solutions (acetonitrile, DMF, propylene carbonate, ethanol, 2-propanol, ethylenegricol, acetylacetone) were measured using a falling ball viscometer[18].

Figure 4 shows the concentration dependence of the t_R for the various solutions indicated in the figure. The electrolyte only contained LiBF$_4$ as mentioned. The t_R decreases with the increasing concentration of the solutions in the range from 0.010 M to 1.0 M for all the solutions. Since the thickness of the EDL formed near the interface between the electrolyte solution and semiconductor becomes smaller with increasing concentration, the time required to form the EDL becomes shorter, which leads to shorter t_R. Only for the DMF solution, was the response of the drain current measured at 5.0 M due to the high solubility of LiBF$_4$ in DMF. We found that the t_R at 5.0 M became higher than that at 1.0 M. We noticed that the viscosity of the solution is apparently increased when the concentration was greater than 1.0 M. Figure 5 shows the viscosity of the DMF solution of LiBF$_4$ plotted as a function of the concentration. An increase in the viscosity at the higher concentration was observed. The viscosity of the 5.0 M solution was 10 times higher than that of the 1.0 M solution. This is because the interaction between the ions and solvent molecules become stronger, and the same mechanism should make the t_R longer, as observed. There must be an

optimal concentration that gives the minimum t_R. In the present work, we have experimentally determined the optimum concentration for LiBF$_4$ / DMF.

As for the other solvents, the solubility of LiBF$_4$ was not high enough to make the effect of viscosity to the t_R prevail over the effect of concentration (reduced double layer thickness). We consider that this tendency ‐ the t_R first decreases as a fuction of concentration and then increases if the solubility can become high enough ‐ is generic.

The relationship between the viscosity and t_R was extensively measured for various solvents and the results are summarized in Fig. 6. The concentration of the electrolyte solutions was fixed at 1.0 M because the t_R of the 1.0 M solution is the lowest for all the solutions investigated in this study. We believe that the tendency obtained below is not strongly affected by the concentration. It was noted that even if the viscosity is the same, the t_R differs with the kind of solvents and that the solvents in Fig. 6 can be categorized into three types based on the intensity of the solvation. They are a complex-forming solvent, nonprotic solvents, and protic solvents. The complex-forming solvent (acetylacetone) has the highest t_R due to the strong interaction between the ions and the solvent molecules. Protic solvents have a middle-strength interaction and the nonprotic solvents have weakest interaction. Therefore, the t_R of the nonprotic solvent is the lowest.

4. Conclusions

The transient characteristics of EDL capacitors and EDL-FETs were investigated. The EDL capacitors cannot be interpreted as simple CR series circuits, which indicated that the response time (t_R) of the EDL-FETs is not merely a result of a simple CR product. Therefore, the t_R of EDL-FETs was measured for various kinds of electrolyte solutions.

The t_R of the EDL-FETs was measured using Si as the active semiconductor. The values of t_R strongly depend on the concentration of the electrolyte solutions. When the concentration becomes larger in the range from 0.010 M to 1.0 M, the t_R decreases. However, when the concentration increases in the range from 1.0 M to 5.0 M for DMF, t_R increased. This result means that the t_R depends not only on the concentration, but also on the viscosity. Furthermore, the kind of solvent influences the t_R due to the strength of interaction between the ions and solvent molecules. In order to shorten the t_R, a solvent with a weak solvation should be used at the optimal concentration.

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Table 1: Fitting parameters of transient characteristics of EDL capacitors (Fig. 2) and EDL-FETs (Fig. 3) using LiBF$_4$/DMF electrolytes of different concentrations.

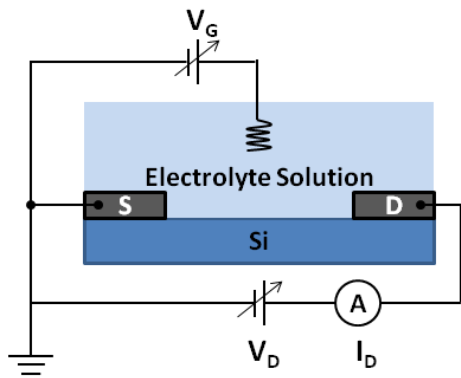| Concentration	EDL capacitors			EDL-FETs
	t_1	t_2	t_3	t_R
0.01 M	1.1 µs	13 µs	350 µs	1.8 ms
0.10 M	1.4 µs	25 µs	6.9 ms	190 µs
1.00 M	1.5 µs	22 µs	390 µs	91 µs

Figure captions

Fig. 1: Setup to measure drain current transients of EDL-FETs. The setup for the EDL capacitors is similar, but the source (S) and drain (D) electrodes are not separated.

Fig. 2: Charging current transients of EDL capacitors using DMF solution of LiBF$_4$ as the electrolyte. The fitting using three exponential functions with different time constants are shown as solid and dashed lines.

Fig. 3: (a)(b) Source current transient of an Si EDL-FET for 0.010 M LiBF$_4$ DMF solution when (a) $V_D = $ -0.5 V and (b) when $V_D = 0$ V, from which the I_D transient can be evaluated (see text). Responses of I_D for LiBF$_4$ solutions when concentration was (c) 0.010 M, (d) 0.10 M, and (e) 1.0 M are also shown. Time zero of Figs. 3(a)-(e) represent the time when the measurement started by the oscilloscope. The raw data points are shown as dots and the fitting curves to the exponential function are shown as solid lines.

Fig. 4: Concentration dependence of t_R for various kinds of solvents. LiBF$_4$ was used as the solute.

Fig.5: Concentration dependence of viscosity for DMF solution of LiBF$_4$.

Fig.6: Response time plotted versus viscosity showing the clear category of solvents, *i.e.* complex forming, protic, and nonprotic solvents.

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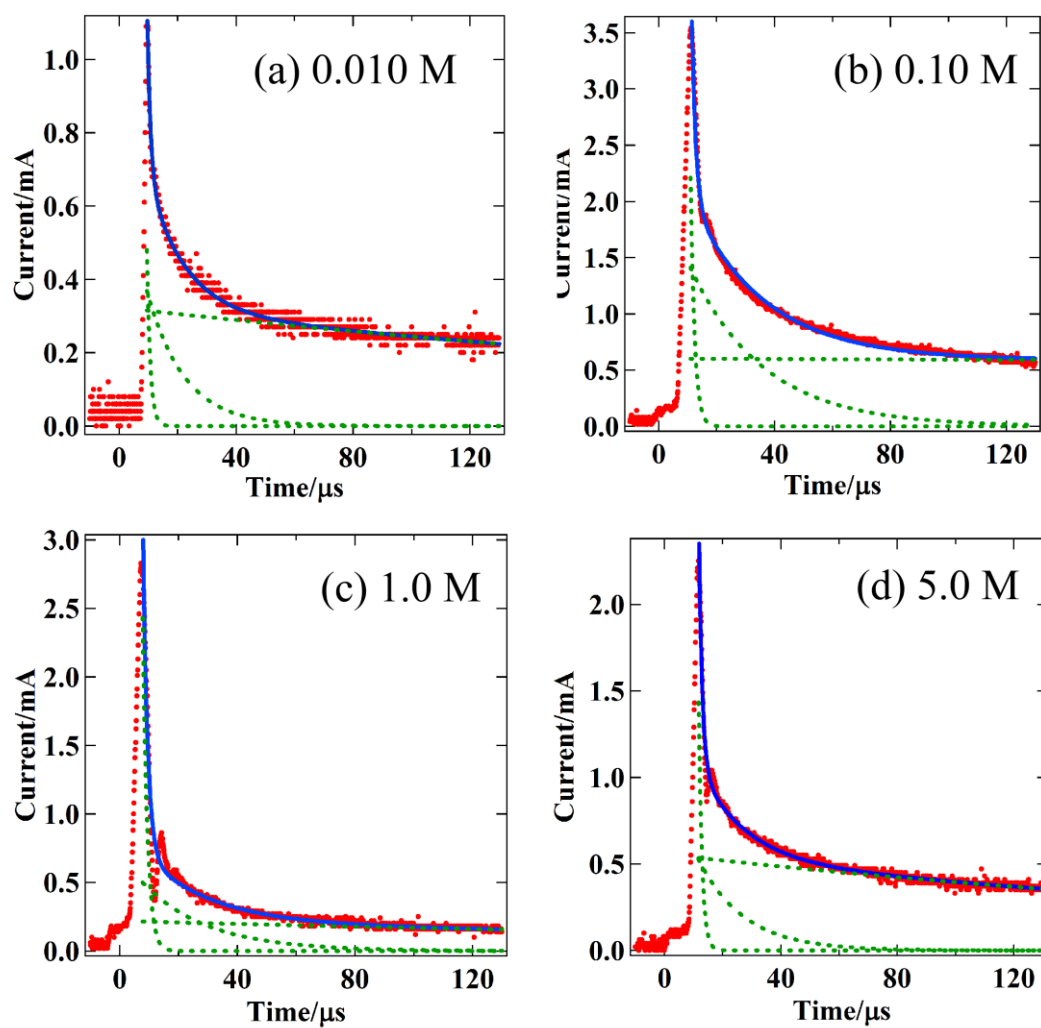
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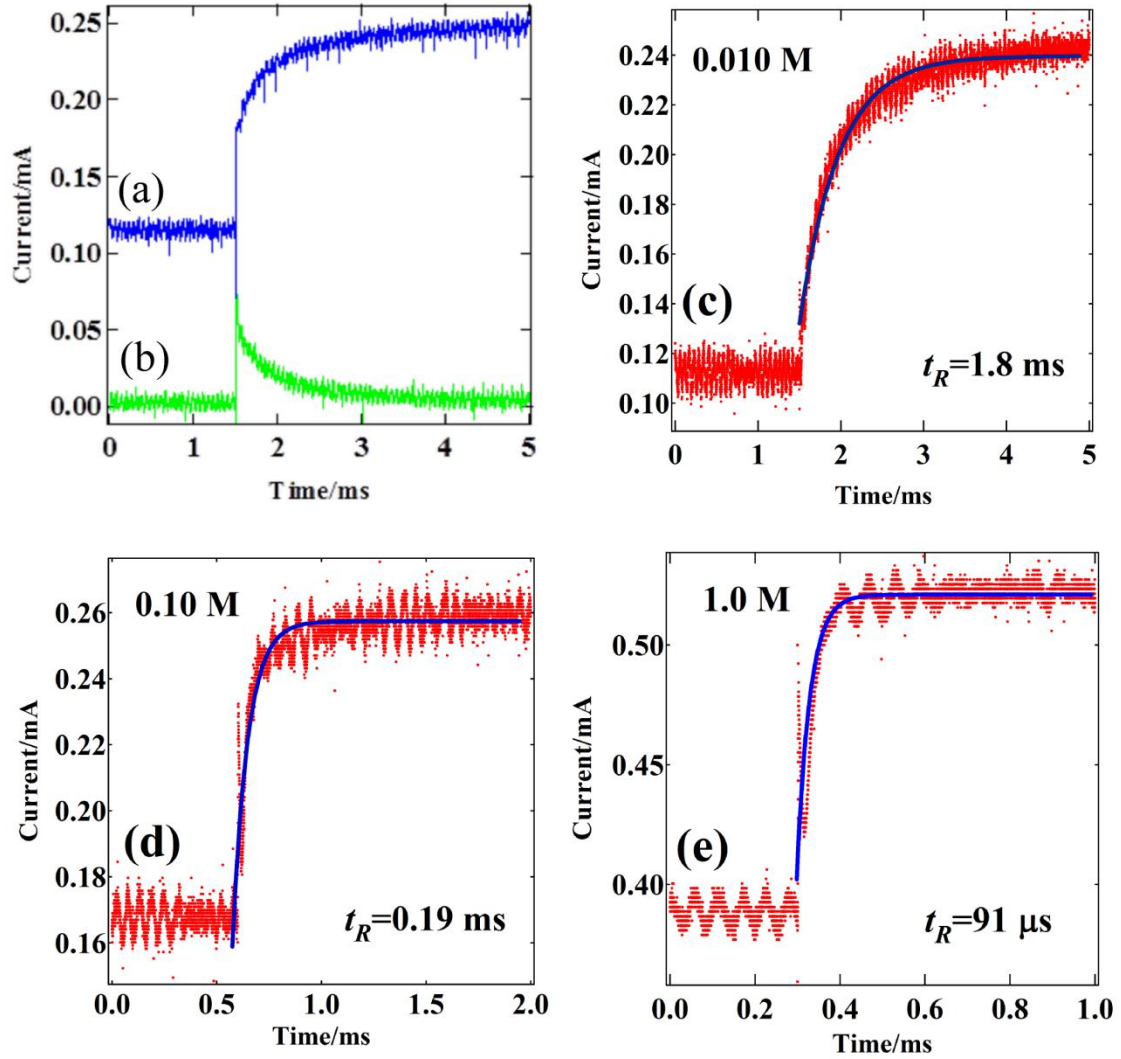
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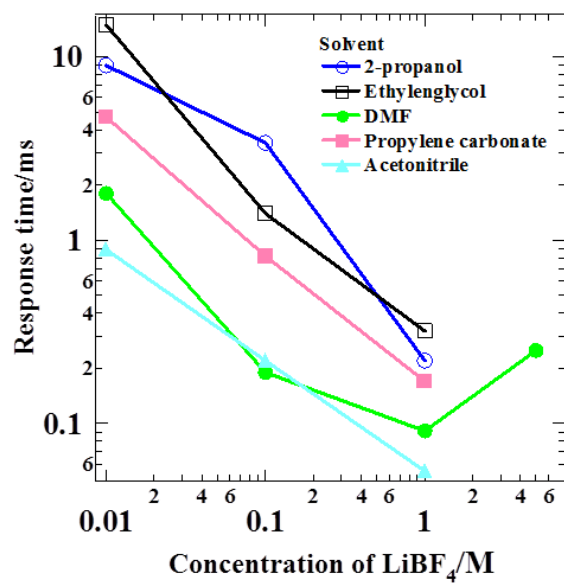
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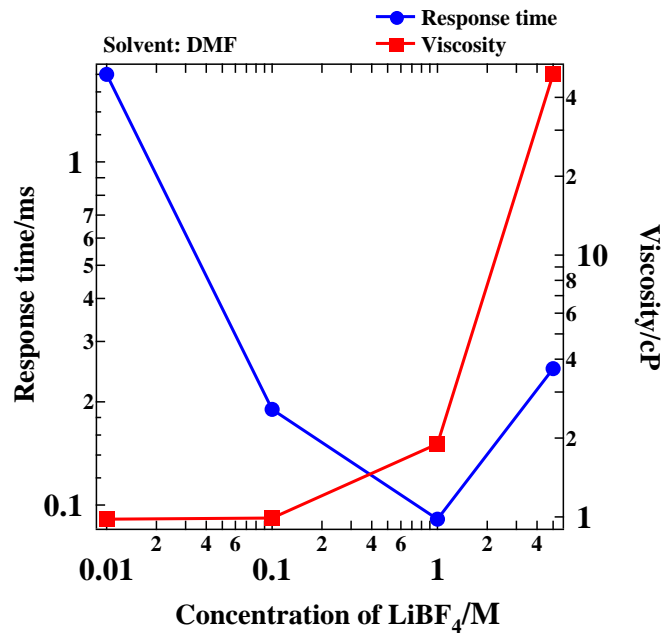
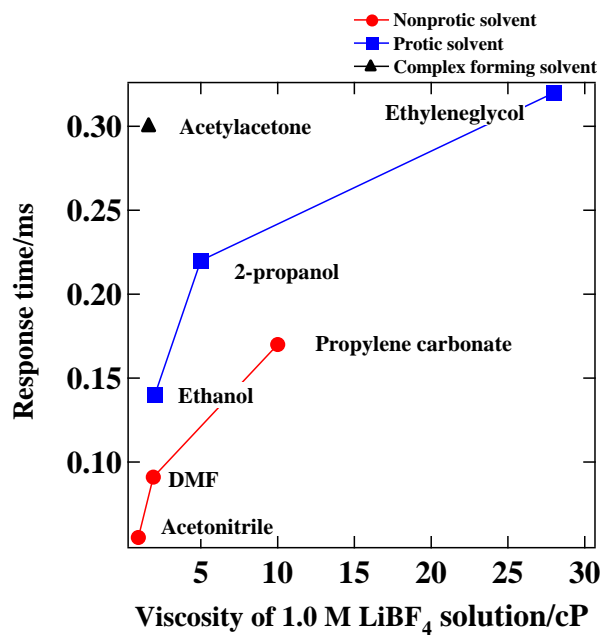Fig.5: Concentration dependence of viscosity for DMF solution of LiBF₄.

Fig.6: Response time plotted versus viscosity showing the clear category of solvents, *i.e.* complex forming, protic, and nonprotic solvents.